VOL. XVIII. [APRIL, 1896.] NO. 4.

AMERICAN CHEMICAL JOURNAL.

THE ACTION OF LIGHT ON SOME ORGANIC ACIDS IN THE PRESENCE OF URANIUM SALTS.[1]

BY HENRY FAY.

HISTORICAL.

The early history of photo-chemical reactions is involved with the history of photography. Schulze in 1727 proved experimentally that the darkening of silver salts is due to the action of light, and in 1799 Scheele[2] showed the effects of different parts of the spectrum. It had been noticed several centuries before that silver salts are subject to change, but the work of Schulze was the first conclusive evidence that this change is due to the action of light. In the early part of this century the action of light on plant growth was studied by many investigators who received the incentive from a suggestion made by Priestley.

Certain physical phenomena were early noticed, as the effect on crystallization by Petit,[3] who showed, in 1722, that solutions of potassium nitrate and ammonium chloride crystallize more readily in the sunlight than in the dark. These effects were studied more carefully by Chaptal[4] and Dize.[5] In 1848

[1] From the Author's Thesis, submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy, June, 1895. The work was undertaken at the suggestion of Professor Remsen and carried on under his supervision.

[2] Traité de l' Air et de Feu.

[3] Mèm. de Paris, 1722.

[4] Jour. de. Phys., vol. 34.

[5] Sur la crystallisation, etc., 1789.

Becquerel[1] published his excellent researches on the phosphorescence of the sulphides of barium, calcium, and strontium, but none of these researches threw any light on the chemistry of the reactions caused by sunlight. Photography was being developed in the early part of the century and various effects were noticed, but the chemistry involved was not worked out. During this period many inorganic salts were found to undergo some change when exposed to the sunlight, and in general this change was a reduction, especially if there was an oxidizable organic substance present.

Among the salts most extensively studied were those of uranium. Before taking up the study of the reactions involved when uranium salts are decomposed in the sunlight, it will be well to review the work which has been done on the organic substances which are subject to change when exposed to the light. Many observations have been recorded in which the fact is simply stated that certain substances are sensitive to light, but only in a few cases has the reaction been a clear one. In the cases studied the reactions can be classified under one of these three heads—substitution, direct combination, and polymerization.

Dumas[2] has shown that the hydrogen atoms of the methyl group in acetic acid can be replaced by chlorine when the two substances are brought together in the direct sunlight, forming a substituted acetic acid. Phenomena of a similar nature were brought out by Schramm,[3] who has shown that when aromatic hydrocarbons having a side chain are treated with chlorine in the direct sunlight the substitution always takes place in the side chain.

Under the second head come the researches of Cahours,[4] who prepared perchlormethyl oxalate and formate by bringing together the acids and alcohol in presence of chlorine. When exposed to the sunlight the reaction takes place forming the ethereal salts.

Chastaing[5] exposed acetic and butyric acids with alcohol and by means of titration was able to measure the rate of etherification.

[1] Ann. Chim. Phys. [3], **9**, 257. [2] Ann. Chim. Phys. [2], **73**, 77.
[3] Ber. d. chem. Ges., **18**, 350, 606, 1272; **19**, 212. [4] Compt. Rend., **23**, 1070.
[5] Ann. Chim. Phys. [5], **11**, 145.

Somewhat similar are the facts discovered by Klinger,[1] who showed that aldehydes have the power of combining with phenanthrenequinone. He also noticed that if a reducible substance is exposed to light in presence of an oxidizable one, the solvent is oxidized while the substance in solution is reduced. By this means Klinger was able to convert phenanthrenequinone into phenanthrenehydroquinone, and at the same time the solvent, ether, was oxidized to acetic aldehyde. He found that benzil in ether solution passed over into a substance which he called benzil-benzöin on account of the ease with which it can be broken down into these two substances. He represents the decomposition by the equation,

$$C_{28}H_{22}O_2 = 2C_6H_5.CO.CO.C_6H_5 + C_6H_5.CHOH.CO.C_6H_5.$$

Under the head of polymerization come the facts discovered by Lemoin.[2] He found that chloral and styrolene are polymerized when exposed to the sunlight. Similar facts have been noticed in the field of inorganic chemistry as in the case of phosphorus and sulphur. Yellow phosphorus is converted into the red modification, and a solution of sulphur in carbon bisulphide deposits the insoluble modification.

The work of Tyndall[3] on light reactions cannot be placed under any of these heads as the nature of the reaction is not known. He exposed the vapor of amyl nitrite to a beam of light and found that there was decomposition; oxides of nitrogen were formed but the other products were not examined. Tyndall also found that allyl iodide and isopropyl iodide are effected by light, but he did not study the subject from its chemical side.

Oxalic acid has been extensively used in photo-chemical reactions, especially in form of its salts, and it has been recommended as a means of determining the amount of sunlight. Döbereiner[4] proposed to use ferric oxalate as a photometer in which the ferrous oxalate or the carbon dioxide given off could be measured. He also found that oxalic acid will reduce platinum chloride to metal, and that silver oxalate is partially reduced to metal.

[1] Ann. Chem. (Liebig), **249**, 137. [2] Compt. Rend., **93**, 514.
[3] Proc. Roy. Soc., **17**, 92, 104. [4] Schweigger's Jour., **62**, 90.

Eder[1] used as a photometer a solution of ammonium oxalate and mercuric chloride, which, on exposure to sunlight, gives off carbon dioxide and deposits mercurous chloride according to the equation,

$$2HgCl_3 + (NH_4)_2C_2O_4 = 2HgCl + 2NH_4Cl + 2CO_2.$$

Having reviewed briefly the effects of light on certain organic substances, the history of the reactions which involve the use of uranium salts will be given in detail. The first person to find that uranium salts are sensitive to light was Bucholz,[2] who described (1805,) certain effects produced by the sulphate and alcohol. He says: "Uranium sulphate dissolves in 25 parts of alcohol, and the solution undergoes remarkable changes on exposure to the sunlight; the yellow liquid becomes turbid and deposits a grayish green substance. After several days exposure the solution acquires an odor of nitric ether; the filtrate is colorless and contains no uranium; the precipitate of a green color and retains sulphuric acid." Bucholz further observes that an ether solution of uranyl nitrate becomes green on exposure to sunlight, and a black substance is deposited.

Chemists added little to these results until Ebelman,[3] in 1831, took up the subject. He confirmed the results of Bucholz with the uranium sulphate and alcohol, but noticed in addition that green crystals were formed, which he said were uranium protoxide. The precipitate he called the bi-basic sulphate of the protoxide, and gave it the formula $2UO.SO_3 + 2H_2O$.

Uranium oxalate was also investigated by Ebelman. He observed that a solution of uranyl oxalate decomposed into a brown substance, which he believed to be the hydrated oxide, and into carbon dioxide and carbon monoxide in changing proportions.

St. Victor and Corvissart,[4] working on the action of light on organic substances, noticed that if a solution of oxalic acid is exposed to the light it will quickly reduce a gold solution. They heated to boiling a four per cent. solution of oxalic acid

[1] Wein. Academy Ber., **2**, 1879. [2] Ann. Chim. Phys. [1], **56**, 142.
[3] Ann. Chem. (Liebig), **43**, 294.
[4] Compt. Rend., **21**, 00; Ann. Chem. (Liebig), **43**, 114.

with a one per cent. solution of uranyl nitrate, finding that in the dark no decomposition would take place, but after exposing to the sunlight action soon began. They say that carbon monoxide was given off, but do not mention having obtained any carbon dioxide. Another fact of interest discovered by them was that a small quantity of uranyl nitrate increased tenfold the action of light on any amylaceous matter, converting it into dextrin and glucose.

Seekamp[1] repeated the work of St. Victor and Corvissart and found that, after a solution of uranyl nitrate and oxalic acid had been exposed to the light for some time, there was a deposit of a green crystalline powder, the solution became colorless and showed an acid reaction. The acid was identified as formic acid by means of its lead and barium salts. From succinic acid he obtained carbon dioxide and propionic acid and the precipitate which was formed, he believed, to be uranous succinate. Butyric acid and carbon dioxide were obtained from pyrotartaric acid.

H. C. Bolton,[2] in a review of the work done on uranium salts in photochemical reactions, adds some interesting facts discovered while working with certain uranium salts in photographic processes. He obtained a salt which is the double oxyfluoride of uranium and potassium, having the composition represented by the formula $2UO_2F + 3KF$. A solution of this salt acidified with formic acid decomposes in the sunlight, forming a precipitate which gives the formula $4UF+KF$. Oxalic acid causes a similar reduction but with the formation of Ebelman's violet hydrate. Solutions of the nitrate, sulphate, oxychloride, and oxyfluoride are reduced when mixed with glycerin and placed in the sunlight. Even in the dry state the uranium ammonium citrate was found to be sensitive to light.

Wisbar[3] next took up the study of light on uranium salts. He verified Seekamp's work on pyrotartaric acid and showed in addition that butyric acid in presence of uranium salts breaks done into propane and carbon dioxide.

Somewhat similar to the work of Wisbar is that of Louis

[1] Ann. Chem. (Liebig), **122**, 113. [2] Amer. J. Sci. [2], **48**, 206.
[3] Ann. Chem. (Liebig), **232**, 262.

Lucien Bonaparte,[1] who obtained a decomposition of valeric acid by exposing it with a solution of uranyl valerate. The products formed he believed to be uranous valerate, and gases which he believed to be carbon dioxide, carbon monoxide, and a hydrocarbon.

Chastaing[2] studied the effect of the red and violet rays of the spectrum on solutions of uranyl nitrate and alcohol and noticed the odor of aldehyde, which is probably the odor Bucholz took for *nitric ether*. Some uranyl acetate was formed in the solution.

At the suggestion of Prof. Remsen, H. C. Jones, working in this laboratory, undertook some time ago the study of the action of light on oxalic acid in the presence of uranium salts. As the results of his work have not been published, a short account of the results which he obtained will be given.

He verified the statement of Seekamp that, in the presence of uranium oxalate, oxalic acid is broken down into carbon dioxide, carbon monoxide, and formic acid. The equation given by Seekamp to express the reaction, is

$$UO_2(C_2O_4) + 2H_2C_2O_4 = U(C_2O_4)_2 + 2CO_2 + 2H_2O.$$

Seekamp[3] thought that the green compound precipitated was uranous oxalate, of the composition $U(C_2O_4)_2.6H_2O$.

A series of experiments was made by Jones in which varying amounts of uranyl oxalate and oxalic acid were used. The amount of carbon dioxide found in every case agreed to within a few cc. with the amount of carbon dioxide which would have been liberated from the oxalic acid used, had it decomposed directly into carbon dioxide, carbon monoxide, and water. The amount of carbon monoxide set free, plus the amount combined as formic acid, was always somewhat less than the carbon dioxide.

The composition of the precipitate formed was found to depend on the amount of uranyl oxalate, relatively to the free oxalic acid originally used. In all cases where a very large excess of oxalic acid was not used, it could be clearly seen that the precipitate was a mixture of crystals and an amorphous mass.

[1] J. prakt. Chem., **30**, 308. [2] Ann. Chim. Phys. [5], **11**, 145.
[3] Ann. Chem. (Liebig), **122**, 115.

Analyses of the precipitate formed from various mixtures confirmed the belief that the precipitate was a mixture. When a solution containing three grams of uranyl oxalate and thirty grams of oxalic acid had been exposed to the light for a time it was noticed that green crystals were forming on the bottom and sides of the flask. The solution was then removed from the direct sunlight, and allowed to stand in diffused light for some time, when a considerable quantity of the crystals was obtained free from impurities. An analysis of the crystals dried between filter-paper gave 45.05 per cent. uranium, which agreed fairly well with the composition $U(C_2O_4)_2.6H_2O$, which requires 45.8 per cent. of uranium, on the basis U = 240, C = 12, O = 16.

Finally, a solution was prepared containing 3 grams uranyl oxalate and 45 grams oxalic acid. Pure crystals were obtained, as described above, which contained 46.05 per cent. of uranium. It thus appears that the crystalline compound is formed pure only when a very large excess of oxalic acid is used.

It was then hoped that, by using a large amount of uranyl oxalate relatively to oxalic acid, the amorphous compound might be obtained in pure condition. For this purpose a solution containing 2 grams of uranyl oxalate and 2 grams of oxalic acid was exposed to the light. A greenish mass was at first precipitated, which, on longer exposure, became purplish-brown. A solution of uranyl oxalate exposed alone to the direct sunlight apparently underwent the same transformation.

It was found further, that a very small amount of uranyl oxalate will decompose a very large, if not an unlimited amount of free oxalic acid, if exposed *continuously* to the direct sunlight. If not continuously, the crystalline compound will separate out of the solution and the action will cease. Thus the reaction suggested by Seekamp, and given above, cannot express the whole truth, since, according to it, 1 molecule of uranyl oxalate can decompose only 2 molecules of free oxalic acid.

The uranyl salt seems to act in some way as an oxidizing agent, as is indicated by the fact that the product precipitated

is some reduction-product of the uranyl compound originally used.

Decomposition of Oxalic Acid in the Presence of Uranyl Oxalate.

As the nature of the precipitate formed when oxalic acid is exposed to the sunlight in presence of uranyl oxalate was not cleared up by Jones on account of lack of time, it was decided, at Prof. Remsen's suggestion, to continue the work and study the products of decomposition. For this purpose, solutions containing oxalic acid and uranyl oxalate in varying proportions were exposed to the direct sunlight, and in all cases it was found that after considerable gas had been given off the solution became cloudy, and then deposited a light green crystalline powder. When all of the oxalic acid was decomposed, and the evolution of gas had ceased, the remainder of the uranium in solution was deposited as a flocky, purplish-brown substance. Evidently, concordant results could not be obtained by working with the precipitate as a whole, and it was decided to remove the light green-colored precipitate when first formed.

To obtain it 3 grams uranyl oxalate and 2 grams oxalic acid were dissolved in a liter of water, and exposed to the direct sunlight. When some of the green precipitate first formed had settled to the bottom of the flask it was filtered off, washed with water, and then dried between filter-papers. The dry substance has a very pale green color, and showed no tendency to oxidation or change of any kind.

The uranium was determined by heating the substance in a porcelain crucible and weighing as the oxide U_3O_8. In all of the analyses made this method was used; frequently, however, the oxide formed was converted into the nitrate and the nitrate again decomposed. This was done simply to control the results, as the oxide U_3O_8 is more readily formed from the nitrate than from the uranium salt of organic acids.

The green-colored substance gave these results:

I. 0.2637 gram substance gave 0.1776 gram $U_3O_8 = 57.17$ per cent. U.

II. 0.2015 gram substance gave 0.1369 gram $U_3O_8 = 57.68$ per cent. U.

III. 0.2560 gram substance gave 0.1725 gram $U_3O_8 = 57.20$ per cent. U.

Calculated for $U(C_2O_4)_2$, 57.69 per cent U.

This shows the substance to be uranous oxalate. It can be obtained at any time, provided the solutions be continuously exposed to the sunlight, and not too large an excess of oxalic acid be present. It was shown by Jones that, when a large excess of oxalic acid is present, and the solution removed after a short exposure to the light, there is a strong tendency to the formation of the crystalline product $U(C_2O_4)_2.6H_2O$. If the solutions are exposed until all of the oxalic acid is decomposed, some of the purplish-brown substance is then formed.

Desiring to obtain the purplish-brown precipitate in pure condition, several attempts were made to get it from solutions containing oxalic acid and uranyl oxalate by removing the uranous oxalate formed and subsequent exposure, but in all cases the precipitate contained a mixture of the two precipitates. When uranyl oxalate in solution is exposed to the sunlight, the same purplish-brown precipitate is formed, and it was decided to use the uranyl oxalate alone for the purpose of obtaining it.

Decomposition of Uranyl Oxalate.

Four grams of uranyl oxalate were dissolved in a liter of water, and the solution filtered to get rid of a small amount of undissolved substance. The solution was exposed to direct sunlight, and within five minutes after exposure the clear yellow solution had become cloudy. The cloudiness increased rapidly. In half an hour there was a deposit of the purplish-brown substance on the bottom and side of the flask nearest the source of light. There was no evolution of gas.

Thinking that possibly the solution held the gas, several attempts were made to collect any gas formed by attaching large tubes filled with uranyl oxalate solutions to nitrometers containing mercury. Under much reduced pressure, and even by gentle heating, it was impossible to collect

any gas. The precipitate formed in the above solutions was filtered off, washed with water, and left to dry in the air. The brown substance on drying changed to yellow, so that it was impossible to prepare it in this way for analysis. Even on drying rapidly between filter-papers there was some change noticed. If the brown substance is allowed to stand in the flask in which it is precipitated the same change takes place, although not so rapidly. The filtrate was always neutral to litmus, and contained nothing but traces of uranium salts which were thrown out on evaporation to small volume. It was impossible in any case to get the uranium precipitated entirely, although the portion remaining in solution was extremely small in comparison with the whole amount of uranium present.

Determination of Uranium in the Brown Precipitate.

Some of the freshly prepared substance was partially dried between filter-papers, transferred to a porcelain boat, and then dried at 100° in a stream of dry hydrogen. The substance, prepared in this way, has a pale, grayish-green color, resembling somewhat uranous oxalate, and in this condition shows very little tendency to pass over into the yellow substance. It was weighed rapidly, placed in a combustion-tube and heated in a current of oxygen. When heated under these conditions, the substance begins to glow, and the combustion spreads rapidly throughout the mass. After a very few minutes the substance is changed into the oxide U_3O_8. The boat is then withdrawn and weighed. The oxide obtained in this way is of a pale olive-green color, and appears to be perfectly pure. The uranium was determined in 6 separate specimens in this way.

I.	0.4768	gram	gave	0.4407	gram	U_3O_8 =	78.47	per cent. U.
II.	0.2373	"	"	0.2180	"	" =	77.99	" "
III.	0.1372	"	"	0.1249	"	" =	78.00	" "
IV.	0.1556	"	"	0.1414	"	" =	77.15	" "
V.	0.1856	"	"	0.1699	"	" =	77.58	" "
VI.	0.1454	"	"	0.1314	',	', =	77.41	" "

Average for the 6 determinations, 77.76 per cent. U.

These results, it will be seen, are fairly concordant, but good results could not be obtained for carbon.

Several attempts were made to determine the percentage of carbon, but, on account of the relatively small amount present, the results were not satisfactory. The substance, when heated alone, gives off small amounts of carbon monoxide, but even by passing the gases over ignited copper oxide, good results were not obtained. The yellow substance, into which the brown one passes on standing, gave better results. These will be spoken of later. Various attempts were made to isolate the acid contained in this salt, but without success. The substance dissolves readily in hydrochloric, sulphuric, and nitric acids, forming green solutions, from which ammonia precipitates the black uranous hydroxide. All that can be said at present in regard to this salt is that it is a reduction-product of uranyl oxalate. There can be no doubt that it contains a small percentage of carbon, as will be made more evident when the yellow transformation-product is considered. Ebelman believed it to be a hydrated oxide, but the presence of carbon proves this assumption to be wrong. Bolton obtained the same precipitate by exposing a solution of the double oxyfluoride of uranium and potassium acidified with oxalic acid. He however did not analyze the product. If this were the simple hydrated oxide, it seems that it should also be formed with other acids than oxalic acid, especially when the same salt of Bolton is acidified with formic acid. In this case only the salt $4UF + KF$ is formed.

Analysis of the Yellow Substance Obtained from the Purplish-brown Precipitate.

The best way to prepare the yellow salt is to allow the brown substance to stand in a desiccator for four or five days. It is also formed when allowed to stand in the air, but it is more convenient to use the desiccator, as in this way the yellow salt can be obtained in dry condition having constant weight. For the analysis of this salt, it was dried to constant weight over sulphuric acid or by heating in an air-bath to 100°. The substance is also formed when the brown precipitate is allowed to stand under water for several weeks. A prelimi-

nary test for carbon was made by heating the substance in a tube through which pure air was drawn. The gases were passed into barium hydroxide solution. There was considerable barium carbonate formed, showing carbon to be present.

This substance was heated in a combustion-tube as in the previous case, and the uranium oxide afterward weighed, the uranium, carbon, and hydrogen being thus estimated in the same operation. The substance was first converted into a brick-red substance, probably U_3O_8, and on higher heating gave the oxide U_3O_8.

Different preparations gave the following results on analysis:

	U.	C.	H_2O.
I.	75.46 per cent.	1.36 per cent.	8.58 per cent.
II.	75.40 " "	1.02 " "	8.04 " "
III.	75.10 " "	1.2 " "	8.50 " "
IV.	74.9 " "	1.15 " "	8.7 " "
V.	75.44 " "	....	....

These results are selected from a much larger number of analyses, all of which agree very closely with the ones given.

It is difficult to account for the small amount of carbon present, but as none of the carbon was given off in the original decomposition, and the brown substance does not lose any carbon dioxide in drying, it is safe to say that all of the carbon is in combination with the uranium. In what form it exists it is impossible to say, as the substance dissolves in acid without separation of any organic acid. If all the uranium is precipitated and the filtrate separated, there is no evidence of any organic substance remaining behind.

Formation of Formic Acid in the Decomposition of Oxalic Acid.

Jones showed that the equation of Seekamp, representing the decomposition of oxalic acid by uranyl oxalate, does not express the reaction, as it does not account for the formic acid nor for the carbon monoxide. It was thought advisable to make a few experiments to see whether formic acid can be built up from carbon monoxide and water in presence of uranium salts. For this purpose the following experiments were made:

I. A 250 cc. Erlenmeyer flask was filled with a solution of

uranyl oxalate, and about 100 cc. carbon monoxide introduced into it. The inverted flask was connected with a long tube bent twice at right angles to show the pressure. The flask was exposed to the direct sunlight. Within two hours the decomposition of the uranyl oxalate was complete The precipitate was the same as the one spoken of above when uranyl oxalate decomposes. No free acid was detected in the solution.

II. Carbon monoxide and water were exposed for fifteen days in the direct sunlight. On examination, at the end of this time, the water was perfectly neutral.

III. Mixtures of equal values of carbon moxoxide and carbon dioxide, in the presence of water, were exposed to the direct sunlight, but no formic acid was obtained.

From these experiments it is shown that the formic acid obtained in the decomposition of oxalic acid is from the oxalic acid itself, and not from the combination of carbon monoxide and water.

Decomposition of Malonic Acid.

The study of malonic acid was next taken up, and it was my purpose to proceed as in the case of oxalic acid, but unexpected difficulties arose.

Uranyl malonate was prepared by bringing together hot concentrated solutions of malonic acid and uranyl nitrate. It separates in a few moments as a bright yellow crystalline powder, adhering firmly to the sides of the beaker. It is nearly insoluble in water and alcohol, more readily soluble in nitric acid, and easily soluble in a solution of malonic acid.

On analysis it gave the following results for uranium:

Calculated for $CH_2<\begin{matrix}COO\\COO\end{matrix}>(UO_2)\cdot 3H_2O$, 56.06 per cent.

0.2526 gram gave 0.1656 gram U_3O_8 = 55.65 per cent. U.
0.3682 " " 0.2416 " " = 55.70 " " U.

Heated to 110° for 4 hours it lost 9.15 per cent. H_2O.

Calculated for $2H_2O$, 8.78.

At 180°, 0.2670 gram lost in weight 0.0325 gram = 12.16 per cent. H_2O.

Calculated for $3H_2O$, 12.6 per cent. H_2O.

This, like many uranium salts, loses some water readily, but loses the last molecule only at high temperatures.

As this salt is almost insoluble in water, it could not be used in this work. Accordingly, dilute solutions of uranyl nitrate and malonic acid were exposed to the light, but within a few minutes the uranyl malonate was completely precipitated. The uranyl malonate dissolves in potassium malonate, and it was hoped to use such a solution for the decomposition. The double salt of potassium and uranium was made by dissolving the uranium malonate in the required amount of potassium malonate. On evaporation, well-formed but small, very bright yellow crystals were obtained. Solutions of this salt, with and without free malonic acid, were exposed to the sunlight for several days, but there was no indication of decomposition in either case. They seemed to be perfectly stable in the brightest sunlight.

The same results were obtained when the uranyl malonate was dissolved in malonic acid and the solution exposed. The malonic acid decomposes when a dilute solution of uranyl oxalate and malonic acid is exposed to the sunlight, but the rate of decomposition is so extremely slow that it was not considered advisable at the time to carry the work further.

Decomposition of Succinic Acid.

Attempts were made to decompose succinic acid by means of uranyl succinate, but so far it has been impossible to effect such a decomposition.

Uranyl succinate is described in Watts' Dictionary as being made from uranyl nitrate and acid sodium succinate by evaporation to dryness. This method was tried, but the uranium salt obtained was so nearly insoluble in water that it was not suited for the experiments. Some of the salt obtained was dissolved in a dilute solution of succinic acid, and this solution exposed to the direct sunlight for some days showed no tendency to change. Various other methods were tried for the purpose of making uranyl succinate, but they were not successful. Solutions of uranyl nitrate and succinic acid can be evaporated to crystallization, but they crystallize separately. It was also hoped to get it from barium succinate

and uranyl sulphate. These salts were brought together in molecular proportions, but part of the barium was changed into sulphate and part into the insoluble barium uranate.

As it was desired to study the decomposition of succinic acid in the presence of uranyl succinnate, the experiments were carried on further.

Seekamp[1] found that succinic acid decomposes in the sunlight in the presence of uranyl nitrate into carbon dioxide and propionic acid. This was verified qualitatively. The action takes place rather slowly, and as this work could be carried on only during the winter and early spring months, it was not carried further. Seekamp believed the green precipitate in this case to be uranous succinate. A small amount of this substance was obtained and analyzed for uranium, but the percentage did not agree with that required for uranous succinate.

It is necessary to do much more work on the precipitates obtained in these decompositions as they are difficult to obtain in a pure state, and, from analyses made of precipitates from other acids, they do not appear to be the simple reduction-product.

Decomposition of Tartaric Acid.

When tartaric acid and uranyl nitrate are exposed to the sunlight, the clear yellow solution gradually turns to a deep green color, and after a few hours there is a precipitation of a light green salt. No gas is given off in the reaction. Several solutions were attached to nitrometers containing mercury, but there was no change in the volume, although the solutions were under much reduced pressure. Heat facilitates the precipitation very greatly. Some of the green solution from which the precipitate had been removed was placed on a water-bath, when there was a complete precipitation in a few minutes. The precipitate is most readily formed when one molecule of uranyl nitrate is exposed with one molecule of tartaric acid. If the solution in which the precipitate has been formed is allowed to stand in the sunlight for several weeks, the green-colored salt passes into solution forming an amber-colored liquid.

[1] Ann. Chem. (Liebig), **133**, 253.

For analysis the green salt was dried between filter-paper and then over solid potassium hydroxide. It gave the following results:

I.

0.2631 gram gave 0.1529 gram U_3O_8
0.2631 " " 0.0555 " H_2O
0.2631 " " 0.1396 " CO_2

II.

0.2949 gram gave 0.1713 gram U_3O_8
0.2949 " " 0.0684 " H_2O
0.2949 " " 0.1662 " CO_2

	Calculated for $U_4H_{12}O_{16}$.	Found. I.	II.
Uranium.....	49.58	49.3	49.31
Hydrogen.....	2.48	2.34	2.57
Carbon	14.87	14.46	15.3

The nature of the above precipitate cannot be learned from the above results, and the formula suggested has no significance at present. It may be possible to isolate the organic portion of the salt, but until this has been done it would be useless to speculate in regard to the nature of the precipitate.

Decomposition of Isobutyric Acid.

Wisbar[1] has studied the action of sunlight on butyric acid in the presence of uranium salts, and found that it is decomposed into propane and carbon dioxide. It was thought desirable to know whether the other acids of this series undergo a similar decomposition, and accordingly a study was made of isobutyric, propionic, and acetic acids. The study of isobutyric acid was taken up first, as it was found to work readily, giving off gas freely when exposed to the sunlight with uranyl nitrate.

Experiments were first made to see whether any definite relations existed between the gases given off. Carbon dioxide was shown to be present by its ready absorption by potassium hydroxide, and the residual gas was burnt from the capillary tube of the nitrometer in which it was collected. It burned with a smoky flame, showing it to be a hydrocarbon.

It was believed that the isobutyric acid would decompose in

[1] Ann. Chem. (Liebig), **262**, 232.

the same way as the butyric acid, giving equal volumes of propane and carbon dioxide. This was found to be the case as is shown by the following experiment:

I. For the purpose of collecting the gases the solutions were exposed in small test-tubes 13 × 120 mm. connected by means of a capillary tube to a nitrometer filled with mercury. The acid to be used was weighed directly into the tube, and a weighed portion of uranyl nitrate was added. Water was now added to bring the solution to the required height in the tube.

2.0201 grams isobutyric acid and 0.3365 gram uranyl nitrate were dissolved in 30 cc. water and exposed to the sunlight. Gas begins to be given off about fifteen minutes after the exposure is made. After being exposed for nearly an hour the lower half of the solution becomes cloudy, and small drops of a dark green, viscous liquid soon appear, which gradually collect in the bottom of the test-tube. Most of the gas evolved seems to come from this large drop. This dark-green, heavy liquid is, however, not always formed, and its formation depends on conditions which have not as yet been learned. A precipitate, however, is always formed—either this liquid or a light green powder.

The exposure was continued for several days when all action ceased. All of the uranium was precipitated.

The total volume of gas was 30 cc. and of this 14.8 cc. were absorbed by caustic potash, which shows half the volume of gas to be carbon dioxide. This also shows that the total decomposition of the acid was approximately 30 per cent. of that calculated for the equation,

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.COOH = CH_3.CH_3.CH_3 + CO_2.$$

At the end of the first day's exposure 21.5 per cent. of the decomposition had taken place.

II. This experiment was carried on precisely as the preceding, except that, after the reaction had begun, a tube filled with warm water was placed around the tube containing the solution. This increased the reaction very much, and it was found that by this method large quantities of the gases can

be collected in a very short time. Of 27 cc. gas collected 13.6 cc. were absorbed by caustic potash.

III. In this experiment much larger quantities of acid and uranyl nitrate were used for the purpose of securing a pure specimen of the hydrocarbon for analysis. After 25 cc. of the gas had been collected, it was removed from the nitrometer so as to get rid of any oxygen or nitrogen, possibly held in solution by the water. This was repeated several times before a sample of the gas was collected for analysis.

The gas was removed by having it under pressure by means of the pressure-tube connected with the nitrometer, and then opening the glass stop-cock of the nitrometer only a little way. The stop-cock was closed before all of the gas had escaped, thus making sure that no air could enter. By this means it was found possible to collect the evolved gas. On absorption exactly half of the volume was shown to be carbon dioxide. The remaining portion was then transferred to a eudiometer and exploded with oxygen.

Volume of original gas.....	21.3 mm.	= 1	volume.
Volume after addition of oxygen	400.7 "	= 18.81	"
Volume after explosion.....	335.9 "	= 15.76	"
Contraction		= 3.05	"

The calculated contraction for C_3H_8 is three volumes. This shows the hydrocarbon to be propane, and the reaction is to be represented by the equation,

$$C_4H_8O_2 = C_3H_8 + CO_2.$$

Decomposition of Propionic Acid.

Uranyl nitrate and propionic acid, when exposed to sunlight decompose very readily, giving off gas in a few minutes after exposure is made. It was found best to use a rather strong solution of the acid. The gas is given off evenly and continues until nearly all of the acid is decomposed. The gas was collected and analyzed in the same manner as described under isobutyric acid.

I.	32.4 cc. of gas gave	15.8 cc. CO_2.	
II.	30.5 " " " "	15.1 "	"
III.	26.4 " " " "	13.2 "	"

These figures show that approximately half the volume of the gas is carbon dioxide.

The residual portion was run into a eudiometer and exploded with oxygen.

Volume of original gas.....	19.97 mm.	= 1	volume.
Volume after addition of oxygen	201.12 "	= 10.07	"
Volume after explosion	147.44 "	= 7.38	"
Contraction.....		2.69	"
Calculated contraction for C_2H_6		2.5	"

This shows the hydrocarbon to be ethane, and the decompositian of propionic acid is to be represented by the equation,

$$C_2H_5.COOH = C_2H_6 + CO_2.$$

Decomposition of Acetic Acid.

Various attempts were made to decompose acetic acid in the same manner as propionic, and isobutyric acid, but it was decomposed only with difficulty. The only proportions which were found to give off gas was when 15 cc. glacial acetic acid and 5 cc. strong solution of uranyl acetate were exposed. From this solution gas was given off, but only extremely slowly. The exposure was made in April and May, about six weeks being required to give enough for analysis. The clear yellow solution did not to any extent change to the green, so characteristic in all the other cases. There was a slight green color, but it was not marked.

Analysis of gas—

13.4 cc. of gas gave 6.4 cc. CO_2.

Volume of original gas	13.2 mm.	= 1	volume.
Volume after addition of oxygen	108.24 "	= 8.2	"
Volume after explosion	80.52 "	= 6.1	"
Contraction.....		2.1	"

Calculated contraction for CH_4 is two volumes, while that found is 2.1 volumes, which shows the gas to be methane, and the decomposition is to be represented by the equation,

$$CH_3.COOH = CH_4 + CO_2.$$

It is interesting to note that the power of decomposition ceases with acetic acid, which breaks down under the influence of light only with difficulty. The power is apparently

lost in formic acid, and it has been impossible so far to effect any decomposition of this acid by light in the presence of uranium salts.

Comparison of the Rates of Decomposition of Propionic, Butyric, and Isobutyric Acids.

For the purpose of comparing the relative rates of decomposition of these three acids, tenth-normal solutions of each were made, and varying quantities of the acid were exposed with varying quantities of uranyl nitrate. It was decided to use propionic acid as the standard in determining the best conditions possible. The following table shows the comparison between two solutions of propionic acid exposed under exactly similar conditions.

No. of days.	Hours of exposure.	Amount of gas collected. No. 1.	No. 2.	Condition of weather.
1	2	0.8	0.6	Clear.
2	7½	2.8	2.8	"
3	7½	3.4	4.8	"
4	7½	4.0	7.2	"
5	15	4.3	9.2	"

Solution No. 1 contained 10 cc. of one-tenth normal nitrate, $UO_2(NO_3)_2.6H_2O$ and 10 cc. one-tenth normal propionic acid.

Solution No. 2 contained 15 cc. one-tenth normal propionic acid and 5 cc. one-tenth normal nitrate, $UO_2(NO_3)_2.6H_2O$.

It will be seen that the solution containing the larger amount of acid acted the more rapidly. The comparison is not exactly fair, as the precipitate which is formed some time after the decomposition begins has some effect, as will be seen in the following table, in which is given a comparison of propionic, butyric, and isobutyric acids. Each solution contains 15 cc. one-tenth normal acid and 5 cc. one-tenth normal nitrate, $UO_2(NO_3)_2.6H_2O$.

No. of days.	Amount of gas collected. Propionic.	Isobutyric.	Butyric.
1	1.2	1.4	1.0
2	2.5	3.0	2.5
3	4.0	4.7	3.6
4	5.3	5.7	4.3
5	5.3	5.7	4.3

No. of days.	Amount of gas collected. Propionic.	Isobutyric.	Butyric.
6	6.5	6.4	4.9
10	7.6	7.4	5.8
11	8.8	8.4	....
12	10.2	9.5	....
13	12.0	10.6	9.0
14	13.6	11.4	9.6
15	15.0	12.4	10.5
16	15.8	12.8	11.2
17	16.3	13.0	11.2

It will be seen that on the sixth day the amount of gas collected from the propionic acid and the isobutyric acid is practically the same. Up to this time there was only slight cloudiness in the solutions, but after three days of rain a precipitate was found in the solution containing isobutyric acid. From this time on it will be seen that there is a gradual gain in the amount of gas collected from the propionic acid over the amount collected from the isobutyric acid.

As the weather was unfavorable for carrying these comparisons any further, the subject was dropped at this point, but it is believed that interesting comparisons can be obtained by working during the summer months.

Summary.

It has been shown that the precipitate in the solution of uranyl oxalate and oxalic acid is formed in two stages: (1) formation of uranous oxalate, (2) formation of the purplish-brown precipitate from the uranyl oxalate left in solution. The nature of the latter has not been cleared up, but it is shown to contain carbon, and consequently cannot be the hydrated oxide as supposed. The formic acid found when oxalic acid is decomposed must come from the oxalic acid itself, as all attempts to build it up from water and carbon monoxide in presence of uranium salts, has failed.

Tartaric acid, when exposed with uranium salts to the sunlight, forms an insoluble precipitate with uranium, the nature of which has not been cleared up.

It has finally been shown that acetic, propionic, and isobutyric acids, decompose into the hydrocarbons corresponding to the acids and into carbon dioxide.

A REVIEW OF SOME RECENT WORK ON DOUBLE HALIDES.

By Charles H. Herty.

The field of the double halides has long been an inviting one for those eager to prepare new compounds with a comparatively small outlay of trouble or thought. This has been due to two causes; first, the ease of formation of the compounds; second, the old idea of molecular combination, according to which any analytical results could be interpreted by the usually accepted formulas. In this way no check was placed upon the work and the result was the description of a large number of compounds and very little effort to deduce any general conclusions bearing upon the constitution of the compounds. More recently chemists have realized that the former so-called explanation, molecular combination, was a mere matter of words sufficing only to cloak ignorance. The realization of this has led to a more careful study of the compounds previously described, and generalizations have been attempted in the line of explanation according to our present conception of valence. Chief among these was the conception of two halogens playing the part of a linking oxygen atom. This theory, though advanced many years ago, received little attention until the recent able paper of Remsen.[1] He found, however, several salts described, whose composition could not be explained in this way. This led to a very careful revision of some of the work of previous investigators, and it was shown that many of the compounds described were incapable of existence, in fact that they were really impure and that little trouble had been taken to purify them.

More recently, Wells[2] has devoted a great deal of time to the systematic determination of the full number of double halides which can be prepared. This work has been characterized by extreme care and wide variations in the conditions of experiment.

Furthermore, many workers have obtained substances by mixing together salts containing different halogens, for example, antimony chloride and potassium bromide. Such substances have been analyzed and formulas deduced. My

[1] This Journal, 11, 291. [2] Am. Jour. Sci., 16, 121. etc.

own work[1] has shown that probably in all cases the so-called mixed double halides containing two halogens are really isomorphous mixtures of different double halides containing only one halogen.

This reaction in the method of work has proved wholesome and has resulted in bringing some order into the chaotic field. But quite recently the old erroneous methods of work seemed to be creeping in again, so that now we find the literature on this subject very confused. It has seemed advisable, therefore, to call attention to the character of some recent work in the hope that further complications may not arise from the acceptance of work which is undeniably bad.

The particular portion of the field to which I desire to call attention is that of the double halides of lead and the alkalies. The French seemed to monopolize this field for many years, during which time a large number of compounds were prepared by Boullay, Ditte, Berthelot, André and others. Working under the direction of Professor Remsen of Johns Hopkins University, I undertook, seven years ago, a revision of the work on the double iodides of lead and potassium. After two years constant work I was able to announce the preparation of only one double iodide of lead and potassium, $KPbI_3.2H_2O$, although all possible variations of conditions of experiment had been made. This reduced the number of compounds of this class from five previously described to one. Soon afterwards, Schreinemakers[2] published a lengthy article on the conditions of equilibrium of solutions of double salts. In this article he accepted Ditte's formula, $PbI_2.2KI$, but changed the amount of water of crystallization. He made no determinations of lead, potassium or iodine in the compound. As soon as his attention was called to the work done by Remsen and me,[3] he made a complete analysis of the compound with which he had been working and found it to be under all conditions $KPbI_3.2H_2O$,[4] thus confirming our work.

Wells[5] next took up the subject and succeeded in preparing

[1] This JOURNAL, **15**, 81, and **16**, 490; and J. Am. Chem. Soc., **18**, 130.
[2] Ztschr. phys. Chem., **9**, 57.
[3] This JOURNAL, **14**, 107.
[4] Ztschr. phys. Chem., **10**, 467.
[5] Am. Jour. Sci., **45**, 121.

only the salt $KPbI_3.2H_2O$, confirming again our work.

In spite of the accumulated evidence on this point, articles continue to appear giving other results. Lenher,[1] in an article on the sulphiodide of lead, speaks of the presence in solution of the salts $PbI_2.2KI$ and $PbI_2.4KI$. No proof of their existence is furnished. As a matter of fact such expressions are simply the result of ignorance of the literature of the subject. No one attempts to defend either of the above formulas at the present day.

Again, Mosnier[2] has published a preliminary notice of some work upon compounds of lead iodide with metallic or organic iodides. Among other compounds he claims to have prepared the salts $3PbI_2.4KI$, $3PbI_2.4NH_4I$. $PbI_2.2NaI$, etc. He gives only general statements upon the conditions of experiment, method of preparation and method of analysis. Furthermore constant reference is made to the work of Boullay, Berthelot, and Ditte, while not a single reference is made to the work of Wells, Schreinemakers, or Remsen and myself. In spite of the very general directions for preparation of the compounds, I have endeavored as nearly as possible to repeat some of the experiments. It was deemed unnecessary to repeat the work upon the salt $3PbI_2.4KI$, for it has been shown repeatedly of late that no such compound is capable of existence. In order to prepare the salt $3PbI_2.4NH_4I$, I followed Mosnier's directions as accurately as possible, and obtained a crystal-mass which by the naked eye was seen to contain a considerable quantity of free ammonium iodide. Inspection under the microscope confirmed this, so that an analysis was deemed superfluous. It has also been found impossible to obtain a specimen of $PbI_2.2NaI$ sufficiently pure for analysis, large quantities of sodium iodide crystallizing out each time with the double iodide. In his article Mosnier states that the details of his experiments will be published later. A year has elapsed, but no details have as yet appeared.

Finally, still another article has appeared, which demands attention. Miss Eleanor Field,[3] as a result of her work, proposed the formulas $3PbI_2.4NH_4I$ and $3PbI_2.4KI$, accurate

[1] J. Am. Chem. Soc., 17, 511. [2] Compt. Rend., 120, 444.

[3] J. Chem. Soc., 1893, 540.

directions being given for the preparation of the salts. As has been stated above, it was deemed unneccessary to repeat the work upon the potassium compound, but the work upon the ammonium compound has been repeated, following the directions to the letter. Crystals were obtained, which under the microscope, seemed very pure. Analysis showed:

	Found. I.	Found. II.	Calculated for $NH_4PbI_3.2H_2O$.
Pb	32.06		32.25
I	59.52		59.32
NH_4	2.68	2.67	2.82
H_2O	5.76		5.61
Total	100.02		100.00

Evidently the salt obtained is $PbI_2.NH_4I.2H_2O$. To show more clearly the incorrectness of Miss Field's formula, I have in the table below placed side by side the analytical data obtained by Miss Field and those obtained by me. As Miss Field analyzed only the salt thoroughly dried at 100°, I have reduced my results also to an anhydrous basis for the sake of comparison. It will be noticed that the total percentage of the elements found by Miss Field in the anhydrous salt is only 96.79, an error of 3.21 per cent.

	Found.	Found by Miss Field.	Calculated for NH_4PbI_3.	Calculated for $(NH_4)_4Pb_3I_{10}$.
Pb	34.02	29.90	34.17	31.65
I	63.16	64.05	62.85	64.67
NH_4	2.84	2.84	2.98	3.68
Total	100.02	96.79	100.00	100.00

By mixing lead iodide and potassium chloride in stated proportions, Miss Field obtained the compound PbICl. Again, from a mixture of lead chloride and potassium iodide she obtained a substance which she called a "double salt," and to which she ascribed the formula $PbI_2.3PbCl_2$. This work I have repeated, following the directions to the letter; in both cases crystals were obtained corresponding exactly to those described by Miss Field. Analytical results show plainly that these substances are not true chemical compounds, but isomorphous mixtures of lead iodide and lead chloride.

	Found by Miss Field.	Found by me.	Found by Miss Field.	Found by me.
Pb	54.80	55.69	64.04	70.18
I	33.70	34.24	18.16	8.10
Cl	9.80	9.61	16.00	21.65
Total	98.30	99.54	98.20	99.93
Atomic ratio Pb : (I + Cl)	1 : 2.05	1 : 2.01	1 : 1.92	1 : 1.99

Retgers[1] has also pointed out that these substances were probably isomorphous mixtures, but no experimental evidence was given.

In conclusion two pressing needs are evident for all work on double halides: first, more care in the preparation of pure compounds; second, more accuracy in analytical work. Surely it is not unreasonable to expect good analyses of such stable compounds as the above with our excellent methods for determining lead, iodine, chlorine and ammonia. Should we not hesitate to deduce a formula from an analysis which sums up only 96.8?

UNIVERSITY OF GEORGIA,
Feb. 10, 1896.

Contribution from the Laboratory of Analytical Chemistry of the University of Michigan.

ON THE QUANTITATIVE DETERMINATION OF HYDROGEN BY MEANS OF PALLADOUS CHLORIDE.

BY E. D. CAMPBELL AND E. B. HART.

In the methods heretofore proposed for the quantitative determination of hydrogen in the presence of methane and other paraffins, this element has been estimated from the contraction after complete combustion by explosion with oxygen, or by partial combustion with air and palladium asbestos, or by direct absorption with spongy palladium.

In some cases, where a large amount of gas is available, the mixed hydrogen and paraffins are burned in presence of red-hot copper oxide, the resulting water and carbon dioxide being collected and weighed in the usual manner.

In 1894, F. C. Phillips[2] proposed the use of palladous chlo-

[1] Ztschr. phys. Chem., **16**, 600. [2] This JOURNAL, **16**, 256.

ride, either dry or in solution, as a reagent for the qualitative detection of hydrogen. Phillips has also shown[1] that palladous chloride is reduced by the olefins and by carbon monoxide, which must therefore be removed before testing for hydrogen. The paraffins, he has further shown,[2] have no action upon palladous chloride, so that hydrogen can be easily detected in their presence. Dr. Phillips proposes the use of dry palladous chloride for the determination of hydrogen, but has not up to the present time overcome the difficulties which he mentions.[3]

Thinking it not unlikely that under proper conditions complete absorption of hydrogen might be obtained by means of a suitable solution of palladous chloride, the authors have devised a method based upon this principle, which they have found very satisfactory. This, with Dr. Phillips' permission, they describe below.

A solution of palladous chloride was prepared as follows: 5 grams of palladium wire were dissolved in 30 cc. of hydrochloric acid, to which was added 1–2 cc. of nitric acid. After solution, this was evaporated just to dryness on the water-bath, redissolved by adding 5 cc. of hydrochloric acid (sp. gr. 1.20) and 25–30 cc. of water, and warming till solution is complete. The solution so obtained was then diluted to 750 cc., giving a nearly neutral solution, containing about 1 per cent. of palladous chloride. This strength of solution was found to be well adapted to the work and was adopted in our subsequent determinations.

The pipette used in the absorption was the ordinary single Hempel absorption pipette, the only modification being in the clamps which fastened the pipette proper to the stand. In place of the small brass bands generally used for holding the glass portion in position, three pairs of small screws were substituted, so that the pipette could be easily slipped from between these when desirable, or firmly retained in position by small wires twisted between each pair of screws. In operating, the amount of solution necessary to fill the pipette is first determined and then introduced into the pipette in the usual manner. The gas to be analyzed, from which every-

[1] *Ibid*, 265–269, and 272. [2] *Ibid*, 262–265. [3] *Ibid*, 262.

thing but hydrogen, paraffins, and nitrogen had been removed by the usual methods, is then passed into the pipette and followed up by sufficient water to fill the capillary completely. The pipette is then disconnected, after first closing the top with a pinch-cock, removed from the stand, and placed in a water-bath for two hours, at the end of which time absorption will be found complete, unless the amount of hydrogen exceeds 65 cc., or the pipette has been previously used, in which case a longer time will be required, as will be seen from the experiments cited below.

A pipette should not be used for the absorption of more than about 100 cc. of hydrogen before refilling with fresh solution. After absorption is complete, the residual paraffins and nitrogen are passed back, when the residual volume may be measured and paraffins determined by addition of oxygen and explosion in the usual manner. After the pipette has been used for the absorption of about 100 cc. of hydrogen, the remaining solution of palladous chloride containing precipitated palladium is rinsed into a casserole and then evaporated just to dryness on the water-bath, 5–6 cc. of hydrochloric acid and 4–5 drops nitric acid and a little water are then added and evaporation repeated. The dry palladous chloride so produced is then dissolved by adding 2 cc. of hydrochloric acid and warming with a small amount of water, and the whole diluted with water to a volume necessary for 1 pipette full. This solution is then returned to the stock bottle, to be used again when needed.

The accuracy of the above method may be judged from the following experiments. In these experiments all volumes of gases given are those found after reducing to standard conditions 0° C. and 760 mm. pressure.

Experiment 1.

Volume of hydrogen taken = 18.7 cc.
" " nitrogen " = 80.3 '

The mixture was passed over 1 per cent. palladous chloride, heated to 50° C. over night; absorption was complete, residue showing 80.3 cc.

Experiment 2.

Volume of hydrogen taken = 53.7 cc.
" " nitrogen " = 23.8 "

1 per cent. palladous chloride was used, and heated in water-bath one hour and thirty minutes. Residue = 23.8 cc. Absorption complete.

Experiment 3. To the residue of nitrogen from experiment 2 was added 26.4 cc. of hydrogen, and the mixed gases returned to the same solution as was used in experiment 2. Heated in the water-bath one hour and thirty minutes, it still showed 6.2 cc. of unabsorbed hydrogen. On again returning the gas to the pipette and allowing it to stand over night in the water-bath, absorption was complete, residue again showing 23.8 cc.

Experiment 4.

Volume of hydrogen taken = 1.07 cc.
" " nitrogen " = 52.23 "

Heated over 1 per cent. palladous chloride in water-bath one hour and thirty minutes, showed absorption of 0.68 cc. On standing over night in water-bath the absorption was 1.21 cc.

Experiment 5.

Volume of hydrogen taken = 1.27 cc.
" " nitrogen " = 70.8 "

This was passed over nearly neutral 2 per cent. palladous chloride and heated on water-bath over night, showing an absorption of 1.23 cc.

Experiment 6.

Volume of hydrogen taken = 60.2 cc.
" " nitrogen " = 18.2 "

Passed over nearly neutral 2 per cent. palladous chloride, and heated in water-bath one hour and thirty minutes. Residue = 18.2 cc.

Experiment 7. Residue from experiment 6 taken, and 64.4 cc. of hydrogen added. Mixture returned to same solution as that used in experiment 6, and again heated in water-bath

one hour and thirty minutes. 4.4 cc. of hydrogen still remained unabsorbed, but, on returning the gas to the pipette the second time and allowing it to stand overnight, absorption was complete, the residue measuring 18.2 cc.

From experiments 5, 6, and 7 it will be seen that a 2 per cent. solution of palladous chloride has very little advantage over a 1 per cent. solution. Further experiments showed that with strongly acid solutions absorption was retarded.

The most satisfactory results have been obtained by using a fresh 1 per cent. nearly neutral solution for each determination; absorption is then complete in two hours. The pipette can be easily refilled with fresh solution, the one which has been used being evaporated down and redissolved and diluted again. 750 cc. of solution will be found to be plenty to keep two pipettes in use, the amount necessary for filling an ordinary pipette being about 160 cc.

ANN ARBOR, MICH., Feb. 11. 1896.

Contributions from the Chemical Laboratory of Harvard College.

XCIII.—ON THE BEHAVIOR OF CERTAIN DERIVATIVES OF BENZOL CONTAINING HALOGENS.[1]

BY C. LORING JACKSON AND SIDNEY CALVERT.

INTRODUCTION.

It is a well known fact that in substituted aromatic compounds the firmness with which atoms of halogen are attached to the benzol ring is diminished by the presence of nitro groups in certain positions, so that these atoms can be replaced by reagents, which would have no effect on them if the nitro groups had been absent. It has also been shown that certain other negative radicals exert a similar loosening effect: these are the two oxygen atoms in substituted quinones—chloranil and bromanil are very reactive bodies—the hydroxyl groups in phenols,[2] and especially in substituted resorcin,[3] and also probably carboxyl.[4] The object of the research described in the present paper was to determine

[1] Presented to the American Academy of Arts and Sciences, May 9, 1894.
[2] Armstrong and Harrow, J. Chem. Soc., 1886, 447.
[3] Jackson and Dunlap, This JOURNAL, 18, 117.
[4] Rahlis, Ann. Chem. (Liebig), 198, 112.

whether such a loosening effect could be produced by less negative radicals, and for this purpose we have taken up the study of derivatives of benzol, in which the substituting radicals are halogens only, so that both the radicals removed and those which make the removal possible belong to this same class, and the latter are distinctly less negative than any of those enumerated above. The amount of work already done in this field is meagre. Balbiano[1] found that paradibrombenzol was converted into parabromphenetol, brombenzol, and a little benzol, when it was heated to 190° with sodic ethylate. The same substance with sodic methylate at 150° gave according to Blau[2] parabromphenol, parabromanisol, and a little hydroquinone dimethylether. Blau[3] also found that symmetrical tribrombenzol gave with sodic methylate at 130° symmetrical dibromphenol and the corresponding anisol as principal products. These results indicate that the atoms of bromine in these di- and tribrombenzols exert some loosening effect, as monobrombenzol must be heated to 200° before it reacts with sodic methylate;[4] but all these actions take place in sealed tubes, and even the maximum difference between their temperatures of reaction and that of monobrombenzol is not very great, only 70°. We decided therefore, in taking up the subject, to try to obtain reactions in open vessels, that is, under conditions which have prevented all action with monobrombenzol, and to do this it was obvious that we must increase the number of atoms of halogen which are to produce the loosening effect. We selected for our first experiment accordingly the tribromiodbenzol having the constitution Br.H.Br.I.Br.H, as in this compound we have iodine as the element to be removed, and this is usually less strongly attached to the ring than bromine or chlorine, and the three atoms of bromine which are to produce the loosening effect are in the most favorable positions for this purpose (two ortho and one para). Trichloriodbenzol would probably have been better, because chlorine is more negative than bromine, but we preferred the bromine compound on account of the great difficulty of preparing the trichloraniline in quantity.

[1] Gazz. Chim., **11**, 401.
[2] Monatsh f. Chem., **7**, 627.
[3] *Ibid*, 630.
[4] *Ibid*, 636.

Upon trying a variety of reagents with the unsymmetrical tribromiodbenzol, we obtained negative results with all except two, sodic ethylate and sodic methylate. These converted it into symmetrical tribrombenzol, melting-point 119°, by replacing the iodine with hydrogen, the sodic ethylate acting to some extent even in the cold, more freely when the solution in alcohol and benzol was boiled under a return condenser, while the sodic methylate did not act in the cold, and only to a limited extent boiling. The unsymmetrical tetrabrombenzol Br.H.Br.Br.Br.H, which differs from the preceding compound only in having an atom of bromine in place of the iodine, was also partially converted into symmetrical tribrombenzol by boiling with sodic ethylate, but there was much less action than with the iodine compound, the tetrabrombenzol undergoing about as much substitution when the solution was boiling, as was the case with the tribromiodbenzol in the cold. The tribromchlorbenzol Br.H.Br.Cl.Br.H, on the other hand, was entirely unaffected by a solution of sodic ethylate in open vessels. These experiments show that the presence of the three bromine atoms exercises a loosening effect similar to to that exhibited by nitro groups, although much weaker in degree. They also furnish an additional case in which the stability of the aromatic compounds of the different halogens increases in the order iodine, bromine, chlorine. This is worth noting, because Körner[1] states that the halogens are removed from dinitrohalogenbenzols (X 1, NO_2 2, NO_2 4) in exactly the reverse order; that is, chlorine most and iodine least easily.

We next turned our attention to the tetrabrombenzol melting at 174–175°, which has been proved by work done in this laboratory to have the symmetrical constitution Br.Br.H.Br.Br.H, as in this substance only two of the bromine atoms are in the positions to the one to be removed (ortho and para) which had proved effective in the unsymmetrical compound. This, however, did not affect the result materially, as this tetrabrombenzol was converted into tribrombenzol (unsymmetrical Br 1, Br 2, Br 4) by the boiling solution of sodic ethylate to about the same extent as the unsymmetrical

[1] Gazz. Chim., 4, 323, note.

tetrabrombenzol. In separating the small quantity of tribrombenzol formed from the large amount of unaltered tetrabrombenzol we have obtained excellent results in both the cases just mentioned by exposing the mixture for a long time to the lowest temperature at which anything sublimes. The sublimate thus obtained, if not the pure tribrombenzol, could be converted into it by a single repetition of this rough fractional sublimation.

An arrangement of the bromine atoms entirely different from the effective ortho para positions is found in the symmetrical tribrombenzol Br.H.Br.H.Br.H, as here all the halogen atoms are in the meta position to each other, but, as has been already mentioned, Blau found that one of the atoms of bromine was removed by the action of sodic methylate at 130°. As our work just described has shown that sodic ethylate is more active than the methylate, we thought this might act even in open vessels, and on trying the experiment have found that sodic ethylate in boiling alcoholic solution removes from symmetrical tribrombenzol a portion of its bromine. The organic products of the partial reaction were oily, but, as the object of our experiment was to determine whether a reaction took place, and not what its products were, no attempt was made to examine them. This is not the only case in which one of three radicals in the symmetrical position has been removed, as Lobry de Bruyn[1] has converted symmetrical trinitrobenzol into dinitranisol or dinitrophenetol by the action of the sodic alcoholates in open vessels. The work of Blau and Lobry de Bruyn, therefore, establishes this as a general behavior of symmetrical compounds, and such replacements are the more remarkable, because a single negative radical has no effect upon one other in the meta position.

In the work with unsymmetrical tetrabrombenzol, mentioned above, it was only the fourth atom of bromine (in the diortho para position to the others) that was replaced by hydrogen, but in some work upon the corresponding dinitro compound $C_6Br_4(NO_2)_2$, done some years ago by W. D. Bancroft and one of us, this atom of bromine remained obstinately

[1] Rec. d. Tr. Chim., 9, 208; 13, 149.

unattacked when other atoms of bromine were removed ;[1] in the same way the reduction of tetrabromdinitrobenzol with tin and hydrochloric acid gave monobromphenylene diamine, so that in these cases the symmetrical atoms of bromine alone were removed, and the action was exactly the reverse of that obtained with tetrabrombenzol and sodic ethylate. This difference is explained by the facts that in the tetrabrombenzol the three atoms of bromine in the trimeta position are the loosening radicals, whereas in the tetrabromdinitrobenzol they are those which are loosened. In this connection we decided to try the action of sodic ethylate on tetrabromdinibenzol, as this experiment had not been included in the previous work of W. D. Bancroft and one of us, and we found that tetrabromdinitrobenzol ($Br.NO_2.Br.NO_2.Br.Br.$) was converted by the action of a cold solution of sodic ethylate into the tribromnitroresorcine diethylether melting at 101°, and first obtained by W. H. Warren and one of us[2] by the action of sodic ethylate on tribromtrinitrobenzol. This substance has the formula $C_6Br_2NO_2(OC_2H_5)_2$, and must have been formed in this case by the replacement of one nitro group and the fourth atom of bromine by ethoxy groups, just as it was formed from the tribromtrinitrobenzol by the replacement of two nitro radicals by ethoxyls. If the action with the tetrabrom body is analogous to that with the trinitro compound, there should be formed at the same time by a parallel reaction a substituted phloroglucine, in this case dinitrobromphloroglucine or its ethers; but although we have found indications that such a substance is formed, we have not succeeded in isolating it.

The principles governing the replacement of radicals attached to the benzol ring, which we have brought forward in this introduction, make it possible to explain the strange behavior of tribromtrinitrobenzol with sodic ethylate. This action consists in the two following reactions, which take place side by side.[3]

[1] This JOURNAL, 12, 289. Sodium malonic ester gave the compound $C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2$; reduction of this gave bromamidoxindol; aniline gave $C_6Br(NO_2)_2(C_6H_4NH)_2$.

[2] This JOURNAL, 13, 184.

[3] This JOURNAL, 15, 619. Tetrabromdinitrobenzol acts in the same way, as just stated, but for the sake of simplicity of expression, the explanation has been confined to the trinitro body, although it applies equally well to the tetrabrom compound.

$$C_6Br_3(NO_2)_3 + 3C_2H_5ONa = C_6(OC_2H_5)_3(NO_2)_3 + 3NaBr.$$
$$C_6Br_3(NO_2)_3 + 2C_2H_5ONa = C_6Br_3NO_2(OC_2H_5)_2 + 2NaNO_2.$$

In this substance we seem to have two zones of action, one consisting of the three symmetrically disposed bromine atoms, the other of the three nitro groups also symmetrically disposed, and the action in each molecule is confined to one of these zones, if it is carried on in the cold. In the first or bromine zone the atoms of bromine are submitted to two loosening influences: (*a*) that of the three nitro groups, in the diortho and para positions to each bromine atom, and (*b*) that of the trimeta bromine atoms on each other. In the second or nitro zone also we have two loosening influences: (*c*) that of the three bromine atoms diortho and para to each nitro group, and (*d*) the loosening effect of the three symmetrical nitro groups on each other. Of these loosening influences (*a*) is by far the strongest, and (*b*) the weakest; it seems therefore that the combined effect of (*c*) and (*d*), of intermediate strength, is about equal to that of (*a*) and (*b*) together; consequently each of these zones of action lies about equally open to the attack of the sodic ethylate, and the two reactions take place simultaneously. When the solvent is alcohol alone, they run to about the same extent. If the repellant action of the three symmetrical nitro groups (*d*) is removed, that is, if tribromdinitrobenzol is used instead of the trinitro body, the nitro groups should be much less loosened than the bromine atoms, and as a matter of fact there has been observed in this case no tendency to remove the nitro groups, the action being confined to the bromine zone, causing the formation of $C_6Br(OC_2H_5)_2(NO_2)_2H$ or $C_6H(OC_2H_5)_2(NO_2)_2H$.

The work described in this paper has furnished us with 3 additional cases, in which atoms of halogens have been replaced by hydrogen under the action of sodic ethylate, but even with these we do not feel that enough facts are known to make it possible to deduce a general rule in regard to the conditions, which produce this curious reaction. The collection of such facts will be continued in this laboratory.

We also tried the action of fuming nitric acid on unsymmetrical tribromiodbenzol, and found that iodine was set free,

and the organic product was the tribromdinitrobenzol melting at 192°, and having the constitution $Br.NO_2.Br.NO_2.Br.H$.

A few statistics which we have collected about the removal of radicals from substituted benzols may be given here. By far the greater number of such removals are those in which a negative radical stands in the ortho position to the radical removed. Of these we have counted over 60 cases, in only 9 of which the negative radical is a halogen. Of the cases of removal, where there is no negative radical in the ortho position, we have found 4 in which a negative radical is in the para position to the radical removed; these are $C_6H_4Br_2$, $C_6H_4ClNO_2$, $C_6H_4BrNO_2$, and $C_6H_4(NO_2)_2$; and to these perhaps should be added five of the nine cases mentioned above, in which the ortho radical is a halogen, as in all of these there is a nitro group in the para position to the radical removed.[1] In no case is a radical removed which is only in the meta position to a single negative radical;[2] but if there are 2 negative radicals in meta positions to the radical attacked (symmetrical tricompound), there are 2 cases in which substitution has been observed, $C_6H_3Br_3$ and $C_6H_3(NO_2)_3$.

Experimental Part.

Behavior of Tribromiodbenzol.

The tribromiodbenzol (I 1, Br 2, Br 4, Br 6) was made from symmetrical tribromaniline by replacing the amido group by an atom of iodine. Silberstein,[3] who discovered this substance, made it from the nitrate of diazotribrombenzol. We have preferred to use the sulphate, and, as our method seems to give a better result than Silberstein's to judge from his statement, we give it in detail. Ten grams of symmetrical tribromaniline were mixed with moderately dilute sulphuric acid in such proportion that there was one molecule of the acid to each molecule of the tribromaniline; the calculated amount of sodic nitrite was then added in small quantities at a time,

[1] In the other cases where a radical was removed, which was ortho only to halogens, these halogens were in the diortho position, and therefore probably were sufficient to cause the removal.

[2] The conversion of meta and para nitranisol into the corresponding nitranilines were not counted, because they took place at such a high temperature, 200°; but perhaps they should be added to the list given above.

[3] J. Prakt. Chem. [2], **27**, 119.

shaking the loosely corked flask after each addition until the red fumes were absorbed. The mixture after standing over night was filtered, and then treated with hydriodic acid till there was no further action. The slightly brown precipitate was washed with water, and purified by crystallization from a mixture of benzol and alcohol, when it showed a melting-point of 104°. Silberstein gives 103°.5. For greater safety it was analyzed with the following result:

0.3374 gram of the substance gave 0.6119 gram of a mixture of argentic bromide and iodide.

	Calculated for $C_6H_3Br_3I$.	Found.
Iodine and Bromine	83.24	83.32

We find the solubilities of the substance the same as those given by Silberstein, but we do not agree with him when he says it sublimes easily, as we have found that it sublimes much less easily than symmetrical tribrombenzol.

To study the action of sodic ethylate on tribromiodbenzol, 6 grams of it were dissolved in anhydrous benzol, and mixed with 40 cc. of an alcoholic solution of sodic ethylate, containing 2 grams of sodium, that is, more than enough to remove all the halogen atoms present. The mixture was then heated on the steam bath under a return condenser for one hour, when the liquid had taken on a dark color, and a brownish precipitate had appeard ; the liquid was now evaporated and the residue treated for half an hour with a large quantity of water, filtered and washed, when it weighed 4.1 grams. Upon subliming this residue, 2 grams of sublimate were obtained in small white needles which melted at 119–120°, the melting-point of symmetrical tribrombenzol. An analysis of the sublimate gave the following result.

0.2612 gram of the substance gave by the method of Carius 0.4695 gram of argentic bromide.

	Calculated for $C_6H_3Br_3$.	Found.
Bromine	76.18	76.51

There can be no doubt, therefore, that the substance is tribrombenzol, formed by the replacement of the atom of iodine in the tribromiodbenzol by hydrogen. The residue which did not sublime was a brownish yellow powder, containing

many black specks. It did not melt at 300°, but melted with blackening when held over the free flame. It was not completely soluble in any of the common solvents, and all our efforts to obtain from it a body fit for analysis have proved fruitless.

The experiment was next repeated under the same conditions, except that the mixture was not heated, but allowed to stand three days at the ordinary temperature. At the end of this time it had turned dark brown, in fact a pale brown color appeared almost as soon as the materials were mixed; the solvents were then allowed to evaporate spontaneously, and the residue treated with water as in the previous experiment, when the aqueous filtrate gave a strong test with starch paste and chlorine water for iodine. The residue insoluble in water was sublimed at a very gentle heat, and crystals of symmetrical tribrombenzol were obtained recognized by their melting-point, 119–120°. The residue, which did not sublime at this gentle heat, was crystalline and of a reddish white color, very different from the amorphous brown product obtained under the same conditions from the action of hot sodic ethylate. The crystalline residue after three recrystallizations from a mixture of benzol and alcohol, showed the melting-point 104°, and was therefore unaltered tribromiodbenzol. It seems, therefore, that cold sodic ethylate behaves like hot, but the acton is less complete.

An alcoholic solution of sodic hydrate, after being warmed for ten minutes with a solution of tribromiodbenzol in benzol, converted it into tribrombenzol with elimination of iodine. This, therefore, acted in the same way as the hot solution of sodic ethylate, but the yield seemed to be larger, and the residue from the sublimation was lighter in color (yellow) and free from black specks. It did not, however, prove to be more manageable than that previously obtained. These differences may be due to the shorter heating, ten minutes in this case instead of an hour when the ethylate was used. Several attempts were made to detect the aldehyde which it seemed probable was formed as the secondary product in the replacement of the iodine by hydrogen, but these led to no definite results.

Sodic methylate when boiled with a benzol solution of tribromiodbenzol for over an hour gives a result similar to that obtained from cold sodic ethylate; that is, tribrombenzol was formed, but there was a large amount of undecomposed tribromiodbenzol. The two substances were separated by careful sublimation and recognized by their melting-points. Cold sodic methylate, on the other hand, gave no action even after standing three days. This was proved by testing the aqueous washings for halogens with negative results, and recovering essentially all of the tribromiodbenzol used.

The following reagents had no effect on the tribromiodbenzol: sodic phenylate in alcoholic solution boiling, sodic hydrate in aqueous solution boiling, sodic carbonate in aqueous solution boiling, zincic oxide and water in a sealed tube at 200° for twelve hours, argentic acetate in aqueous solution boiling, aniline boiling, tin and hydrochloric acid, sodic malonic ester both cold and hot. The proof that no action had taken place in these experiments was obtained either by the recovery of the unaltered tribromiodbenzol, or by tests for a salt of the halogens which gave negative results. In most cases both methods of proof were applied.

To determine whether the removal of the iodine was due to the loosening effect of the three atoms of bromine or to the slight attraction of iodine alone for carbon, iodbenzol was treated with sodic ethylate under the same conditions which had produced an action on the tribromiodbenzol; but after heating the mixture for an hour and a half no test for sodic iodide could be obtained, showing that there had been no action.

Action of Fuming Nitric Acid on Tribromiodbenzol.

When tribromiodbenzol was treated with fuming nitric acid, it lost its white crystalline appearance even in the cold, and became converted into a yellow powder. If the mixture was allowed to stand at ordinary temperatures over night, and then water added to it, iodine appeared both in scales and in the form of vapor, as a great amount of heat was given off. The identity of the iodine was also established by the smell

and the violet color of its solution in carbonic disulphide. If now the insoluble portion was washed with cold alcohol until free from iodine, and then recrystallized several times from a mixture of benzol and alcohol, it showed the constant melting-point 191°, which indicated that the substance was tribromdinitrobenzol, and this was confirmed by the following analysis:

0.3375 gram of the substance gave by the method of Carius 0.4740 gram of argentic bromide.

	Calculated for $C_6HBr_3(NO_2)_2$.	Found.
Bromine	59.26	59.78

The somewhat high results may be due to a trace of a substance containing iodine. If the mixture of tribromiodbenzol and fuming nitric acid was boiled, the organic product was the same, but no free iodine was obtained.

Behavior of Unsymmetrical Tetrabrombenzol Melting at 98°.

The action of sodic ethylate on this substance was selected for study, because that reagent had given the best results in the work on tribromiodbenzol just described. To prepare the unsymmetrical tetrabrombenzol, 20 grams of tribromaniline were dissolved in 180 cc. of hot glacial acetic acid, about 80 cc., that is, a considerable excess of a distilled solution of hydrobromic acid (boiling-point 125°) added, and, disregarding any precipitate formed, the mixture treated with sodic nitrite in the proportion of a molecule and a half or two molecules to each molecule of the tribromaniline. For this purpose the finely powdered nitrite was slowly sifted, with vigorous stirring, into the solution, which had previously been cooled so that it felt barely warm to the hand. The white crystals which were suspended in it gradually changed into a dirty brown solid, much of which dissolved even in the cold. The mixture was then heated for two or three hours on the water bath; the solid matter at first went into solution, but later the tetrabrombenzol, as it formed, separated, principally in long white needles, or sometimes in part as a semi-liquid brown mass. The needles were separated mechanically, and were usually found to be pure. The semi-liquid portion solidified in a short time, and was purified by dissolving it in a

little hot benzol, and pouring this solution into alcohol. The tetrabrombenzol precipitated in this way had a slight reddish color, while the mother liquid was of a dark claret-red. The precipitate was easily obtained white by one or two recrystallizations from a large volume of alcohol, to which it was well to add a little benzol. In this way 20 grams of the tribromaniline gave 22 grams of tetrabrombenzol, instead of the 23.88 grams required by theory, a yield of 92 per cent.

Eight grams of the tetrabrombenzol were mixed with an alcoholic solution of sodic ethylate, made from 2 grams of sodium and 50 cc. of absolute alcohol, and a little benzol to assist the solution of the tetrabrombenzol. The mixture was heated to boiling under a reverse condenser for two days, when it had taken on a blackish green color; it was then evaporated to dryness and washed with water. The wash water gave a good test for sodic bromide. The residue insoluble in water was sublimed at the lowest possible temperature, when a small amount of white needles was obtained, which melted at 119°, the melting-point of symmetrical tribrombenzol. The residue which had not sublimed at the very low temperature used made up the principal bulk of the product, and was chiefly unaltered tetrabrombenzol. This method of fractional sublimation has also yielded us excellent results in another similar case, which will be described later in this paper. The sodic ethylate, therefore, acts on the tetrabrombenzol in the same way that it does on the tribromiodbenzol, replacing by hydrogen the bromine atom occupying the same position as the atom of iodine, but the action takes place with more difficulty, and is less complete.

Behavior of Unsymmetrical Tribromchlorbenzol.

The tribromchlorbenzol was prepared by a method similar to that used for the tetrabrombenzol. Upon adding the hydrochloric acid to the solution of tribromaniline in glacial acetic acid a precipitate of the chloride was formed, but this went into solution as the amido was converted into the diazo compound. Twenty grams of tribromaniline yielded 15 grams of tribromchlorbenzol melting at 82°. Two grams of this substance were heated for four hours with an alcoholic

solution of sodic ethylate, prepared from half a gram of metallic sodium; when upon evaporation to dryness and washing with water only a very faint test for halogens could be obtained from the wash water, and the residue, which consisted of unaltered tribromchlorbenzol, weighed nearly 2 grams. A similar experiment with the tetrabrombenzol, in which the mixture was boiled for only three hours, gave a strong test for sodic bromide and a small amount of tribrombenzol. The chlortribrombenzol, therefore, if effected at all by sodic ethylate, is much less susceptible to the action than either the corresponding iod or brom compound.

Behavior of Symmetrical Tetrabrombenzol.

Tetrabrombenzol, melting at 174–175°, which has been proved by work done in this laboratory to have the symmetrical constitution (1, 2, 4, 5), was boiled for over twelve hours with an alcoholic solution of sodic ethylate; the brown liquid thus obtained, with some long, rather dark colored crystals, which were deposited as it cooled, was evaporated to dryness and the residue washed with water. The wash waters gave a good test for sodic bromide. The residue insoluble in water was then extracted with a mixture of alcohol and benzol, filtered to remove a brown insoluble substance, and the filtrate concentrated, when it deposited crystals which melted at 174–175°, and were therefore the unaltered tetrabrombenzol. The mother liquor was evaporated to dryness and cautiously sublimed at as low a temperature as possible; the crude sublimate melted at 42-43°, and upon resubliming it with the same care its melting-point rose to 44°, the melting-point of unsymmetrical tribrombenzol (1, 2, 4), which must be formed if one of the atoms of bromine is removed from this tetrabrombenzol. Only a small portion of the substance, however, reacts with the sodic ethylate, by far the greater part remaining unaltered.

Experiment with Symmetrical Tribrombenzol.

Blau[1] states that tribrombenzol is converted by sodic methylate into the symmetrical dibromphenol, when the substances

[1] Monatsh. f. Chem., 7, 630.

are heated together in methyl alcohol solution for two or three days at 120–130°. We accordingly tried an experiment to see whether sodic ethylate would have a similar action in open vessels, as we had used this reagent in the preceding work. Ten grams of tribrombenzol were boiled with a solution of the necessary amount of sodic ethylate in about 200 cc. of alcohol for somewhat more than seventy hours; the aqueous wash waters from the product gave a good test for sodic bromide, and in addition to a large amount of unaltered tribrombenzol we obtained a very little of an oil, probably the dibromphenol ethylether, which is a liquid. As this result, which it will be observed confirms Blau, had given us all the information about the reaction which we wished, we did not pursue the work further.

Hexabrombenzol gave when boiled with sodic ethylate a good test for sodic bromide. The organic product was an oil, and a great deal of unaltered hexabrombenzol was recovered. Hexachlorbenzol gave a similar result.

Action of Sodic Ethylate on Tetrabromdinitrobenzol.

In the experiments described in this paper the fourth atom of bromine was removed from tetrabrombenzol by sodic ethylate, while in the work by W. D. Bancroft and one of us[2] upon the tetrabromdinitrobenzol, the fourth atom of bromine was not removed by aniline or sodium malonic ester. It seemed of interest, therefore to try the tetrabromdinitrobenzol with sodic ethylate, and see whether it behaved like the tetrabrombenzol with this reagent or in the same way that it had behaved with the other reagents mentioned above. For this purpose 10 grams of tetrabromdinitrobenzol were dissolved in benzol, and treated with an alcoholic solution of the sodic ethylate made from 2 grams of sodium. The solution became claret-colored as soon as the sodic ethylate was added, but this color changed later to a reddish brown. There was no perceptible evolution of heat. The mixture was allowed to stand at ordinary temperatures for two days, after which it was evaporated spontaneously. The residue, after being washed with water, was recrystallized from alcohol until it

[2] This JOURNAL, 12, 289.

showed the constant melting-point 100° to 101°. This showed that it must be the tribromnitroresorcine diethylether made by Warren and one of us[1] from tribromtrinitrobenzol. This substance must have been formed by the replacement of one nitro group, and the fourth atom of bromine by two ethoxy radicals. To confirm this the wash waters of the original product were tested for a bromide and a nitrite, and good results obtained in both cases. If in this case the reaction has run as with tribromtrinitrobenzol,[2] which we should infer from the isolation of tribromnitroresorcine diethylether, the secondary product should be bromdinitrophloroglucin, or its ethers. As a matter of fact, an oil having the properties of a phenol was obtained by acidifying the aqueous wash waters from the first of the reaction, but all our attempts to bring it into a form fit for analysis have failed, and we have been prevented from continuing work on this substance by the departure of one of us from Cambridge.

Contributions from the Chemical Laboratory of Cornell University.

THE CIS AND TRANS MODIFICATIONS OF BENZENE HEXABROMIDE.

W. R. ORNDORFF AND V. A. HOWELLS.

Benzene hexabromide ($C_6H_6Br_6$), seems to have been obtained first by Mitscherlich,[3] about 1837, by the action of bromine on benzene in the sunlight. This addition-product of benzene, when heated with an alcoholic solution of potassium hydroxide, gave an oily tribrombenzene, which Laurent afterwards obtained in crystals by the evaporation of its ethereal solution.

But little else was known of this substance until 1887, when Meunier,[4] after having carefully studied the hexachlor addition-product of benzene, and shown that it existed in two modifications, which he termed α- and β-, turned his attention very naturally to Mitscherlich's benzene hexabromide, in order to see if it did not exist in two isomeric forms, and also to determine to which of the hexachlorides it corresponded. The method of preparation of the hexabromide was improved

[1] This JOURNAL, **13**, 184.
[2] *Ibid.*, **15**, 619.
[3] Ann. der Phys. Pogg., **35**, 374.
[4] Ann. chim. phys. [6], **10**, 269.

by Meunier, and the complete crystallographic study of the substance, undertaken at his request by Des Cloizeaux, established the isomorphism, and consequently the identity of chemical constitution between this hexabromide and the α-hexachloride of benzene. This conclusion was further supported by the complete analogy shown by the two substances in their chemical conduct. Regarding an isomeric hexabromide corresponding to the β-hexachloride Meunier says nothing.

Friedel,[1] in 1891, published a very interesting paper in which he discusses the constitution of the two hexachlorides of benzene in the light of the stereochemical hypothesis. To the β-modification he assigns the cis formula, because the higher symmetry of the cis structure might account for its comparative stability, higher melting-point and greater specific gravity. As the α-hexachloride crystallizes in the monoclinic system and is always formed in much greater quantity than the β-product, he regards it as a trans compound. He then shows that the cis formula has an hexagonal symmetry and that the β-hexachloride really crystallizes in the hexagonal system being in fact pseudo-regular.

In 1892 Matthews[2] showed that benzene hexabromide could be made by passing air saturated with bromine through a layer of benzene floating on a dilute solution of sodium hydroxide, a method similar to that by which he had previously made the two benzene hexachlorides so readily. Later he found that a better method was to mix benzene and bromine in the presence of water or dilute caustic soda solution. In regard to the product formed by this method he says, "I have not as yet investigated the benzene hexabromide thus produced, but it will be of interest to see whether it is a simple substance or a mixture. Meunier has already examined the hexabromide produced by other processes and finds it to be homogeneous."

It will be seen from this brief survey of the work done on benzene hexabromide that it corresponds with the α- or trans benzene hexachloride and also that the β- or cis modification

[1] Bull. Soc. chim. (Paris), [3], **5**, 130. See also This JOURNAL, **13**, 356.
[2] J. Chem. Soc., **61**, 110.

of benzene hexabromide, predicted by the stereochemical theory and corresponding to the cis hexachloride, has not yet been made. It seemed of interest, therefore, to see if this variety of the hexabromide could be prepared and, if so, to study it in the light of the stereochemical theory and of the facts stated by Friedel regarding the two benzene hexachlorrides.

Experimental.

Benzene hexabromide was first made following Meunier's method exactly, by treating boiling benzene with bromine in the direct sunlight. Hydrobromic acid was evolved in large quantities from the beginning of the operation. The crystals remaining after the excess of bromine and benzene had evaporated off spontaneously, were washed with water, dried, and then repeatedly extracted with boiling alcohol, in which the bromine substitution-products of benzene dissolve readily, while the addition-products are only sparingly soluble. The yield of the crude hexabromide by this method was only 20 grams, though we used 250 grams of benzene and 550 of bromine. Meunier states that he obtained 85 grams of the hexabromide from the above amounts of benzene and bromine. He used the method of sublimation to free his material from substitution-products, however, which may account for the difference between his results and ours.

In our experiments quite a large quantity of paradibrombenzene was formed, but as this substance is soluble in alcohol no difficulty was experienced in separating it from the hexabromide.

The crude benzene hexabromide thus made was then subjected to very careful fractional crystallization, using chloroform as a solvent. Friedel used this method and solvent to separate the cis and trans benzene hexachlorides and obtained excellent results, but notwithstanding all our care we found it impossible to obtain a substance with any higher or lower melting-point than that of Meunier's hexabromide. The crystals in the different fractions were always homogeneous and all had the same melting-point (212–215° C.). The method used by Matthews to separate the two benzene hexa-

chlorides, (distillation in steam, the α or trans product alone being volatile), was next tried, but without success, nothing being volatilized with the steam after ten hours treatment.

As it seemed not improbable, that, at the temperature at which the hexabromide was prepared, the cis compound, if any were formed, might have been transformed into the more stable trans modification, we next made the benzene hexabromide by the method proposed by Matthews, taking care to keep the temperature in the neighborhood of 0° C. 100 grams of benzene were floated on 300 cc. of a one per cent. solution of sodium hydroxide and 650 grams of bromine were added (50 grams daily), from a dropping-funnel. The bromine dissolved in the benzene, forming a heavy red oil, which fell to the bottom of the flask. After the addition of each 50 grams of bromine fresh sodium hydroxide solution was employed. When all the bromine had been added the watery layer was removed and the oil allowed to stand in an open flask in a hood for about eight weeks. There then remained in the flask a mass of beautiful, large crystalline plates together with some benzene, bromine, and monobrombenzene. The contents of the flask were then placed in an open dish and the volatile portion allowed to evaporate spontaneously. The crystals left were ground to powder, extracted with cold alcohol, (to remove bromine monobrombenzene and *o*-dibrombenzene), and then boiled several times with alcohol to remove substitution-products of benzene. This process removed all but 20 grams of the crystals which melted at 205–210° C. The material recovered from the alcohol melted at 85–90° C. and was shown to be principally paradibrombenzene. The product insoluble in alcohol was then put into a paper shell and extracted with chloroform, using a Soxhlet fat-extractor for this purpose. At the end of this operation there was left in the paper shell 0.6 gram of crystals, which melted at 249–252° C. but which after being recrystallized from boiling benzene had a melting-point of 253° C., turning brown and giving off some hydrobromic acid at this temperature. The crystals obtained from the chloroform solution melted at from 205–217° C. After several recrystallizations from benzene, however, they melted at 212–215° C., and probably contained a very small amount of the

higher melting compound. The only other successful attempt to make the crude hexabromide containing enough of the higher melting product to isolate was carried out in exactly the same manner and with the same quantity of materials as the one above described, except that water was used in place of the solution of sodium hydroxide. After removing the substitution-products with alcohol and extracting with chloroform, 0.5 gram of the higher melting substance was obtained. None of this product melting at 253° C. was formed when the bromine and benzene were mixed dry and indeed but little of the hexabromide itself was formed under these conditions. When the bromine was added to the benzene and sodium hydroxide solution or water in the direct sunlight and no precautions were taken to keep the mixture cold, substitution-products mostly resulted, and from the small amount of hexabromide formed no higher melting product could be isolated.

As both these products were prepared from pure benzene directly and both were undoubtedly addition-products, from their chemical conduct, it was not deemed necessary to make complete analyses, so only a determination of the amount of bromine each contained was made. The following are the results obtained by the Carius method.

α-Product Melting at 212–215° C.

0.2182 gram gave 0.4404 gram AgBr.

	Found.	Calculated for $C_6H_6Br_4$.
Bromine	85.91	86.01

β-Product Melting at 253° C.

0.2500 gram gave 0.5032 AgBr.

	Found.	Calculated for $C_6H_6Br_6$.
Bromine	85.65	86.01

These results indicate that both of these substances are hexabrom addition-products of benzene.

Molecular weight determinations were next made with the α-product melting at 212–215° C., using the boiling-point method and the apparatus[1] recently described by one of us for this purpose. The following are the results[2] obtained:

[1] This JOURNAL, 17, 517.

[2] These determinations were made for us by Mr. C. L. Bliss, to whom we wish here to express our thanks.

α-Benzene Hexabromide, $C_6H_6Br_6 = 558$.

Solvent: *Benzene.*

Boiling-point 79.6° at 744.5 mm. barometric pressure.

Molecular elevation for 100 grams 26.6°.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	118.71	1.4083	1.1863	0.060°	739.9	526
2	"	2.6126	2.2008	0.109	739.7	537
3	"	3.4914	2.9411	0.132	739.7	593
4	"	4.3077	3.6287	0.160	739.5	605
						565

Average of all determinations, 565

Molecular weight at infinite dilution, 545

Barometer 740–739.5 mm.

These results show that the molecular weight of the α-product, melting at 212–215° C. is 558 and that the formula of the substance is $C_6H_6Br_6$. Unfortunately it was impossible to determine the molecular weight of the higher melting β-benzene hexabromide as we did not have enough of the material left to give satisfactory results. Owing to the high molecular weight of this substance it requires over a gram, nearly a gram and a half, to give a rise of *six hundredths* of a degree. It seems almost certain, however, from the method of preparation, the analyses and the analogy of the hexabromides with the hexachlorides of benzene that both these addition-products have the same molecular weight and that they are stereoisomers.

Professor A. C. Gill, of the Mineralogical Department of this University, made a complete crystallographical examination of these two substances for us and, since his results with the α-product melting at 212–215° C. differ somewhat from those given by Des Cloizeaux and Des Cloizeaux's measurements vary considerably from the calculated values in some cases, they are given here complete for both substances. The material melting at 212-215° C. was carefully recrystallized several times from chloroform and was undoubtedly much purer than that examined by Des Cloizeaux. The higher melting β-product was crystallized both from benzene and from xylene, in which it is much more soluble.

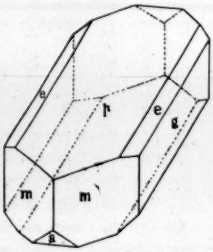
"Two modifications of benzene hexabromide were examined.

The α-hexabromide was found to agree, in general, with the description given by J. Meunier.[1] The angles, however, were found to be somewhat different from the figures given by Des Cloizeaux, and they also agree rather better with each other. Crystals from chloroform, xylene, and from a mixture of the two, were measured. Those from chloroform were brilliant, clear, and colorless. The crystals obtained by a second crystallization from chloroform gave the best results; *viz*:

Monoclinic; $\beta = 69°22'$; $a : b : c = 0.9938 : 1 : 0.5268$ Faces observed; $p = 0P(001)$; $g = \infty \breve{P}\infty$ (010); $m = \infty P$ (110); $a = +2P\bar{\infty}$ ($\bar{2}01$); $e = P\breve{\infty}$ (011); and, on one or two crystals, $b = +P$ ($\bar{1}11$); and $h = \infty P\bar{\infty}$ (100).

In the following table are given some of the more important angles, with the results of Des Cloizeaux for comparison.

			Des Cloizeaux.	
	Observed.	Calculated.	Observed.	Calculated.
p : m	75° 3′		75° 8′	
p : a	122° 16′		120° 33′	122° 25′
m : a	63° 47′			
p : a′	57° 46′	57° 44′	57° 35′	
m : m	85° 57′	85° 51′	86° 36′	87° 14′
m : m′	94° 12′	94° 9′	92° 50′	92° 46
p : e	26° 14′	26° 18′	26° 3′	
g : e	63° 48′	63° 42′	64° 10′	63° 57′
g : m	47° 8′	47° 4′ 30″	46° 23′	
b : a	37° 16′	37° 16′		
p : h	69° 27′	69° 22′		



A common shape of the crystals from chloroform is seen in the accompanying figure, though the development of the clinozone is frequently much less than here shown.

The β-hexabromide of benzene crystallizes in the regular system. Only octahedral planes were measured (on the stage of the microscope), though the rhom-

[1] *Loc. cit.*

bic dodecahedron appears also to be quite frequent in occurrence. Unlike the corresponding hexachloride, the crystals show no trace of double refraction."

Regarding the α-hexabromide, melting at 212–215° C., Meunier's statements were confirmed in every particular.

As to the β-product so small a quantity of the material was left after the analysis that but little could be learned of its properties and chemical conduct. It has a higher melting-point (253° C.), and is less soluble in chloroform, benzene, toluene, and *m*-xylene than the corresponding α-benzene hexabromide. In alcohol and ether it is almost insoluble. It is decomposed quantitatively into hydrobromic acid and the unsymmetrical tribrombenzene when heated with an alcoholic solution of potassium hydroxide.

That the α-benzene hexabromide is the trans compound seems quite certain from the larger amount formed, the system in which it crystallizes, the lower melting-point and the complete analogy of this substance with the trans hexachloride. The smaller amount of the β-compound formed, the crystal form and the higher melting-point, all indicate the cis stereo formula for this modification of the benzene hexabromide. It is worthy of note here, however, that this β-hexabromide is actually regular in its crystal form, while the corresponding hexachloride is hexagonal, being pseudo-regular, as first shown by Friedel, and confirmed by an examination made by Dr. Gill of some of the crystals.

CORNELL UNIVERSITY,
ITHACA, N. Y., January, 1896.

SILICIDE OF CALCIUM.

BY G. DE CHALMOT.

When making silicides of different metals in an electric furnace, I have often used a flux in order to make the mixture that was used more liquid. In cases where I used lime as a flux, I have often found that the resulting silicide contains considerable amounts of calcium. I have thus introduced calcium in copper, silver, iron, and manganese silicide. I tried to obtain pure calcium silicide by putting into the furnace a mixture of silica, calcium oxide and carbon. I have

found that if these ingredients are mixed in such proportions as to give the compound $CaSi_2$, mainly carbide of calcium is obtained, which, however, contains some silicide. If silica is used in excess and the amount of carbon is reduced, a calcium silicide of metallic appearance can be obtained, especially if a direct current of low voltage (25 volts and 225 amperes) is used. This silicide often contains some carbide as can be ascertained by the formation of acetylene gas. It also contains much more silicon and much less calcium than corresponds to the formula $CaSi_2$. All my specimens, moreover, contain some iron. The iron is derived from the furnace, the pencils and the silica (powdered quartz). All the iron which is present accumulates in silicide, because iron silicide is much more readily formed than calcium silicide.

Different samples contained:

	Calculated for $CaSi_2$.	Found. I.	II.	III.	IV.
Si	58.33	71.19	62.48	81.65	91.99
Ca	41.67	19.75	28.41	15.61	5.60
Fe		3.74	2.74	3.61	0.92

Specimens I and II contain calcium carbide, II contains lead colored crystals imbedded in a more or less crystalline matter. III is silver white, homogenous and of crystalline structure. IV has much the same appearance, but is of darker color and contains some graphite. It is remarkable that sample IV was found on the anode, which was the upper pole in this special test. All specimens are hard enough to scratch glass.

The reactions which Wöhler describes[1] for calcium silicide, $CaSi_2$, were obtained with all the specimens.

With cold water some hydrogen is formed, more with warm water. Dilute hydrochloric acid forms a yellow silicic acid, and stronger hydrochloric acid forms a more orange colored acid. Dilute hydrochloric acid and sulphur dioxide form a red compound. I also found that if hydrochloric acid is brought into contact with finely divided silicide, hydrogen silicide is sometimes formed, which is self-igniting, and when burning leaves little white flakes of silica.

[1] Dammer: Anorganische Chemie, [2], 2, 327.

In these specimens calcium silicide, $CaSi_2$, and silicon are mixed. When they are boiled with hydrochloric acid, the calcium silicide is decomposed and crystals of silicon remain. A part of Sample III, which is apparently homogenous, was thus treated. The insoluble residue of silicon and silicic acid was washed by decantation, and the silicic acid was dissolved with hot sodium carbonate solution. The remaining black crystals contained Si 95.88, and Fe 4.25 per cent.

This shows that these crystals contain, in addition to silicon, most of the iron silicide which is only little attacked by boiling hydrochloric acid.

When calcium carbide is heated in an electric furnace with an excess of sand, some crystals are formed, which contain in addition to silicon some calcium silicide that can be detected by the hydrochloric acid reaction.

WILLSON ALUMINUM COMPANY, SPRAY, N. C.

THE CONDUCTIVITY OF YTTRIUM SULPHATE.

BY HARRY C. JONES AND CHARLES R. ALLEN.

The yttrium sulphate used was prepared from a portion of the material previously employed by one of us in determining the atomic weight of yttrium.[1] This is probably the purest yttrium compound thus far obtained containing, according to Rowland, not over, and probably much less than one-half per cent. of impurities. The details of the purification are given in full in the article cited above.

At the end of the atomic weight determinations the yttrium was left in the form of the sulphate with which some of the oxide had been mixed. This mixture was dissolved in a little dilute nitric acid, the yttrium precipitated as oxalate and the oxalate ignited to the oxide.

The oxide thus obtained was treated in small portions with an excess of pure sulphuric acid, and the product evaporated to dryness in an air-bath. It was then heated to constant weight in the same bath, at a temperature a little above the boiling-point of sulphuric acid. The sulphate thus obtained was perfectly soluble in water, and solutions prepared from it were used in the measurements described below.

[1] Jones: This JOURNAL, 17, 154.

200 cc. of a solution of yttrium sulphate containing 0.011957 gram to the cc. were used as the starting-point. The molecular weight of the yttrium sulphate was taken as 466.08, and the volumes were calculated on the basis of one-sixth of this number, or 77.68.

The water used was prepared from ordinary distilled water by redistilling, first from potassium permanganate containing a little sulphuric acid, and then from alkaline permanganate. This water contained no detectable trace of acid or alkali, and gave a conductivity value far less than the probable experimental error of the work.

The Kohlrausch form of apparatus, as recommended by Ostwald,[3] was used. The dilutions were made by withdrawing one-half the contents of the cell and adding an equal quantity of water, using a carefully calibrated pipette.

To reduce the accumulative error which is unavoidably connected with this method of dilution, the process described above was repeated only a limited number of times. Measured volumes of the original solution were then taken, and diluted directly in measuring flasks. Each of the solutions thus prepared, was used as a starting-point for a new series of dilutions made with the pipette.

The values given are the mean of two complete series of conductivity measurements for the various concentrations. Owing to the limited amount of material available, it was necessary to use small volumes in making up the solutions, and to repeat the process of dilution with the pipette more frequently than is compatible with extreme accuracy; hence the results are subject to an error that may possibly amount to one per cent.

In determining the cell-constant we used two $\frac{n}{50}$ potassium chloride solutions made up from different samples. Ostwald's value for μ_v at 25° (129.7) was taken. The cell-constant was redetermined from time to time during the work. The samples of potassium chloride had each been recrystallized six times, and their flame reactions were those of perfectly pure potassium salts.

The results of the conductivity measurements are given in

[3] Lehrb. Bd., 2, 631-633.

the following table. The column headed v gives the number of liters which contains a one-sixth gram molecular weight of yttrium sulphate. That headed μ_v, the molecular conductivities at the volumes v.

Owing to the extreme dilutions, the values in determinations 13, 14 and 15 must be regarded as only roughly approximate.[1]

No. of determination.	v.	μ_v.
1	6.49	23.2
2	12.98	27.8
3	25.96	32.5
4	51.92	38.5
5	103.84	36.9
6	207.68	54.0
7	415.36	66.6
8	830.72	78.8
9	1661.44	102.6
10	3322.88	123.8
11	6645.76	152.6
12	13291.52	192.9
13	26583.00	240.7
14	53166.00	333.3
15	106332.00	601.1

JOHNS HOPKINS UNIVERSITY,
CHEMICAL LABORATORY.

THE PRACTICAL USE IN THE CHEMICAL LABORATORY OF THE ELECTRIC ARC OBTAINED FROM THE LOW POTENTIAL ALTERNATING CURRENT.

BY MILO S. WALKER.

In this paper the author does not claim to have discovered any action of the electric arc that is not already known to chemists, but he will attempt to give a few suggestions as to the way in which the highest temperature at our command can be obtained and used in every chemical laboratory supplied with a fixture for incandescent lighting. Many colleges and secondary schools are equipped with these fixtures, and others can obtain them at but little cost. There is no practical reason why they should not be used for some experi-

[1] The material was purified and the original solution was made up by Jones; the conductivity determinations by Allen.

ments that cannot be performed with a Bunsen burner or a blow-pipe.

The alternating current of about 50 volts and 1 to 5 amperes, now generally used for incandescent lighting, furnishes an excellent arc for chemical experimentation. It is very efficient and can be handled easily and safely even by beginners in laboratory work.

The apparatus required consists of an iron or wooden stand, a screw clamp like those used for holding burettes, insulated copper wire, some electric light carbons, and a rheostat.

A piece of the so-called 10-ampere flexible lamp-cord may be connected at one end with a plug set into the socket intended for an incandescent lamp. The two parts at the other end of the twisted cord are left free. Besides the lamp-cord two pieces of ordinary insulated copper wire of medium size, (about No. 20) and 70 cm. long will be needed. These wires can be supplied and fixed as directed by any dealer in electrical supplies.

The rheostat is the most important part of the apparatus. Any commercial rheostat capable of carrying 12 amperes will answer all ordinary purposes. It may be necessary in large buildings where one transformer supplies 100 lights or more, to use an additional resistance. About 40 feet No. 13 German silver wire has been found very satisfactory in a building where 175 lights are used.

The adjustable rheostat is essential to the proper control of the current, and to prevent too high heating of the wires and consequent melting of the safety fuses when the arc is started. All the experiments are started with a high resistance which is lessened until the proper arc light is obtained.

The assorted carbons are $\frac{1}{4}$ to $\frac{1}{2}$ inch in diameter. The cored carbons are much better than the ordinary uncored ones. For obvious reasons "coppered" carbons should not be used. Carbons differ much in quality. Some contain considerable quantities of carbides and carbonates of metals. Those manufactured for use in optical projection usually contain less of these substances and give the best results.

The operator should not touch any metallic fixtures con-

nected with the earth while he is working with the apparatus, as serious shocks may be received if the transformer is not properly insulated, a defect not uncommon in electrical work. It is better to work at a table on which there are no gas or water fixtures. Gas should be conducted to the table by a rubber tube connected with a gas-cock so far removed that there is no danger of touching any part of the apparatus and the gas-cock at the same time. There seems to be no other danger in working with the 50-volt alternating current. The students working in this laboratory sometimes receive shocks, but they generally consider shocks less disagreeable than accidental burns incident to work in general chemistry.

The electric arc can be used for the following purposes:

1. To show the effect of high temperatures upon difficultly fusible and "non volatile" substances.

2. For reduction of oxides of metal.

3. As a partial substitute for the blow-pipe in qualitative analysis.

4. For the synthetic preparation of some compounds of carbon from the elements.

There is a wide range of experiments showing the effect of the electric arc upon substances almost infusible by other means.

The apparatus can be arranged in a variety of ways depending upon the experiment. For general use it may be arranged thus: Fasten a cored carbon about 10 × 1 cm. in a vertical position so that the lower end is about 10 cm. from the top of the table. Connect by wrapping with insulated copper wire, stripped where contact is made with the carbon. Bore a conical shaped cavity 4 or 5 mm. deep in one end of another piece of cored carbon 4 × 1 cm. Fix into a wooden clamp and connect with insulated wire like the other carbon. On account of the heat an iron clamp with insulated handle is better for some experiments. Connect all wires so that the circuit will be completed if the carbons are allowed to touch each other. As the light is intense the eyes should be protected by a dark or blue glass. The longer carbon is stationary. The movements of the shorter carbon are controlled like a test tube and holder. The rheostat should be adjusted so

that an arc $\frac{1}{16}$ to $\frac{1}{8}$ inch long can pass between the lower end of the longer carbon and the edge of the conical cavity in the smaller carbon. A small piece of the substance to be tested can be placed in the cavity. Most minerals and common metals fuse easily. A piece of quartz 2 × 1 mm. fuses completely. A piece the size of a pea fuses on one side.

As this contribution is intended only to show how the electric arc can be obtained and used in a chemical laboratory, a description of experiments is omitted except where they show the method of working. The apparatus has not been in use long enough to show all its possible applications or even a small part of them. But it has been shown that many of the remarkable experiments of Moissan can be repeated on a smaller scale by this simple apparatus. His work suggests much that can be done in the ordinary chemical laboratory lighted by "incandescent lamps."

If iron, copper or manganese ores are placed in the conical cavity, the metals are formed containing small quantities of carbides.

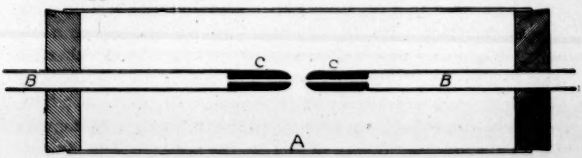
For reduction of oxides it is better to substitute for the solid upper carbon, a carbon tube made by removing the core from the "cored carbon" 3 or 4 cm. long. This tube is then fastened into a brass tube of about the same outside diameter, but with a large bore. The joint can be made gas-tight by a paste of pure graphite and water. The brass tube is fixed and connected with wire like the upper carbon in the other apparatus. The end of the carbon tube should occupy the position of the lower end of the larger carbon as indicated above. Now a gas can be passed through the carbon tube so that it will strike a substance in the cavity of the small carbon, while the arc is passing. Hydrogen or coal gas may thus be conveniently used to prevent oxidation of metals while cooling, and seem to assist in reducing oxides and chlorides while the arc is passing. If carbon dioxide is used, carbon monoxide is formed with apparent increase in the reduction of oxides. In all these experiments a crater is gradually formed, and the arc generally passes from the inside of the carbon tube, thus giving maximum efficiency. When oxygen is used, the crater forms rapidly and enlarges to the full

diameter of the carbon. Carbon monoxide is the main product of the quite rapid combustion, and acts as a powerful reducing agent upon an oxide in the cavity of the other carbon. By reducing with carbon monoxide in this way and cooling in hydrogen, quite pure manganese has been obtained from pure manganese dioxide. Similar experiments with oxides of other metals will be tried as soon as pure materials are secured.

Experiments with the electric arc are particularly interesting to the student, because he is able to get quick, sharp and definite results. The manipulation is so easy that young students can obtain beads of copper, iron or manganese after a few minutes practice. The electric arc has been used in this laboratory as an aid in qualitative analysis and a partial substitute for the blow-pipe, but the method will not be described at present because it has not been sufficiently tested. A special apparatus has been used in which the electric arc is inside a partially closed glass tube, and the volatile constituents of the substance to be treated are collected and partially separated on the sides of the glass. The results so far obtained are very satisfactory.

Some experiments on the synthesis of the hydrocarbons from their elements have been tried. Thus acetylene is easily prepared by the method of Berthelot[1] modified by Dewar.[2]

The apparatus may be made as follows :



Fit a gas tight cork into each end of a straight lamp chimney. Pass brass tubes 1 cm. diameter and 15 cm. long through each cork. Into one end of each tube fix a tube of carbon 3 cm. long, prepared and fitted as shown under experiments for reduction of oxides. The joints of carbon and brass tubes should be gas tight.

[1] Compt. Rend., 84, 640. [2] Proc. Roy. Soc., 29, 188.

Fit the corks and brass tubes so that the ends of the carbon tubes are nearly together, test the apparatus for gas leakage, turn on the current and again test after the heat has reached a maximum. If air-tight pass a stream of hydrogen through the brass and carbon tubes. After the oxygen in the apparatus has been consumed it may be necessary to increase the current.

As there is nitrogen from the air in the apparatus small quantities of hydrocyanic acid are formed at first along with acetylene. The yield of acetylene is not large, but the method seems to be fully as satisfactory as the usual laboratory method of preparation of this gas from coal gas by burning it in an insufficient supply of air. This is recommended as a laboratory method for students. It is the only experiment showing synthesis of carbon and hydrogen from the elements, and the construction and manipulation of apparatus are not too difficult for any one who has had a few weeks' experience in a laboratory.

CHEMICAL LABORATORY, RACINE HIGH SCHOOL,
RACINE, WISCONSIN.

THE PREPARATION OF ALLYLENE, AND THE ACTION OF MAGNESIUM UPON ORGANIC COMPOUNDS.

BY EDWARD H. KEISER.

As described in a previous paper[1] metallic magnesium at a low red heat acts energetically upon the vapors of the alcohols. The metal glows and is converted into a black coherent mass. This black residue, when put into water, evolves a gas which consists chiefly of hydrogen and allylene. The evolution of gas becomes very rapid if a few drops of ammonium chloride solution are added to the water. The hydrogen and allylene can be readily separated from one another by conducting the mixed gases through a series of wash-bottles containing an ammoniacal solution of silver nitrate; the allylene is thereby converted into the insoluble silver allylide, AgC_3H_3, while the hydrogen passes through unchanged.

The best yield of allylene in the earlier experiments was

[1] Journal of the Franklin Institute, January, 1895.

obtained from the magnesium that had been heated in the vapors of propyl or of allyl alcohols. Recent experiments have shown that a more advantageous method of preparing the hydrocarbon is to heat magnesium powder in the vapor of acetone and to decompose the black mass thus obtained with water. In the method of preparation now adopted a layer of magnesium powder is put into a thin-walled iron tube, which is as long as the combustion furnace that is to be subsequently employed for heating it. The iron tube is closed with asbestos stoppers, and through these stoppers glass tubes are passed; so that the acetone vapor may be conducted in at one end of the iron tube and the gases formed during the reaction may be drawn off at the other end. The acetone is converted into vapor by boiling the liquid in a flask which is connected with one end of the iron tube containing the magnesium. After the air is driven out of the apparatus the iron tube is heated in the combustion furnace. At a low red heat the action begins; the magnesium becomes red hot and finally the glowing extends throughout the entire mass of the metal. When this has taken place the contents of the tube are allowed to cool down in the acetone vapor; the black mass is then removed from the tube and, since the moisture of the air acts upon it, it is best to preserve it in a tightly stoppered bottle. To obtain allylene from this residue it is only necessary to put it into a flask containing water to which a few drops of ammonium chloride solution have been added. The gas given off consists mainly of allylene and hydrogen; the latter gas being obtained from the magnesium that has remained unacted upon.

In order to throw light upon the nature of the reaction that takes place when magnesium acts upon the alcohols and upon acetone, the gases that escaped from the tube while the magnesium was glowing, were collected in gasometers over water. These gases were analyzed and the results of the analyses are given in the following table:

Alcohols.	CO_2.	CO.	Unsaturated hydrocarbons.	Saturated hydrocarbons.	Hydrogen.
Methyl	0.8	0.6		19.7	78.9
Ethyl		0.4	14.0	11.1	74.5
Propyl		3.5	17.8	19.9	58.8
Isopropyl		0.2	12.2	15.4	72.2
Isobutyl		0.5	11.4	14.4	73.7
Amyl	1.0		20.4	22.3	56.3
Tertiary amyl (*a*)			24.3	17.5	58.2
" " (*b*)	0.2		22.4	17.9	59.3
Secondary octyl (*a*)		0.5	26.0	24.5	49.0
" " (*b*)	0.6	1.6	25.2	25.8	46.8

From the very small quantities of oxides of carbon in these gases it seems probable that the magnesium combines with the oxygen of the alcohols; hydrogen and hydrocarbons are thereby formed, and at the elevated temperature of the reaction a portion of the magnesium unites with the carbon and hydrogen of these compounds forming magnesium allylide. The black residue contains, besides the magnesium oxide and magnesium allylide, a quantity of free carbon. Attempts have been made to extract the allylide by means of solvents, but thus far it has not been possible to obtain a solvent for it. That magnesium allylide is present in the black mass is shown not only by the action of water upon it, whereby allylene is evolved which has been transformed into the silver, the mercury and the copper compounds which characterize this hydrocarbon; but also by the fact that it contains from 0.3 to 0.4 per cent. of hydrogen, as has been found by burning weighed quantities of it in a stream of oxygen. Further experiments have shown that when the magnesium is heated in an atmosphere containing no hydrogen, as, for instance, in carbon monoxide or carbon dioxide, and the residue thus obtained is decomposed by water, the gas evolved gives scarcely any precipitate with ammoniacal silver solution. The small traces of silver allylide thus obtained being formed from the hydrogen which is occluded in the metallic magnesium.

The black mass consisting of magnesium oxide, carbon, and magnesium allylide obtained by the glowing of magnesium in the vapors of acetone and of the alcohols was in each case

treated with water, and the gases evolved were conducted through an ammoniacal solution of silver nitrate. The silver precipitates were removed by filtration and, after washing and drying, were analyzed. The following table contains the results of the analyses :

Magnesium allylide from		Analyses of silver precipitates. Wt. taken.	Wt. AgCl found.	Per cent. Ag.
Acetone		0.1617	0.1577	73.40
Methyl alcohol		0.1292	0.1270	73.97
Ethyl "	(*a*)	0.1163	0.11365	73.53
	(*b*)	0.0979	0.09615	73.89
Propyl "		0.15605	0.1522	73.39
Isopropyl "	(*a*)	0.27308	0.26802	73.58
	(*b*)	0.10244	0.10114	74.31
Allyl "	(*a*)	0.16705	0.1620	72.97
	(*b*)	0.17185	0.16735	73.27
Isobutyl "		0.1301	0.1289	74.56
Amyl "	(*a*)	0.18156	0.17933	74.34
	(*b*)	0.1365	6.13767	75.90
Tertiary amyl "		0.08509	0.08374	74.07
Calculated for AgC_3H_3				73.45

The comparatively close agreement of these results with the theoretical value for silver in silver allylide indicates that the silver precipitates were most probably pure compounds. The copper allylide was made by conducting the gases from the evolution flask through an ammoniacal solution of cuprous chloride. The greenish yellow precipitate was filtered and washed thoroughly with water and, after drying in desiccators, was analyzed.

Found 62.1 and 62.2 per cent. of Cu.

Calculated for CuC_3H_3, 61.98 per cent.

The mercury allylide has also been prepared. When first formed it is a white flocculent precipitate. It was purified by dissolving it in boiling alcohol. On cooling it crystallized out in the form of slender needles. These crystals possessed the properties of the mercuric allylide described by Kutscheroff.[1]

Experiments have also been made to determine the yield of allylene obtained by this method of preparation. If it be assumed that the magnesium acts upon the acetone vapor according to the following equation :

[1] Ber. d. chem. Ges., **17**, 26.

$$2C_4H_4O + 3Mg = 2MgO + Mg(C_4H_3)_2 + 6H.$$

then the residual magnesium mass should contain 3.3 per cent. of hydrogen. Determinations of hydrogen by combustion gave on an average 0.37 per cent.; so that the yield would be about 0.1 of the theoretical amount. Further, 10 grams of the magnesium residue gave about 0.7 gram silver precipitate.

Further experiments with the allylene are in progress. The gas is readily absorbed by concentrated sulphuric acid. It is probable that a sulphonic acid is thus formed. The sulphuric acid, after having absorbed a large volume of the gas, was diluted with water and neutralized with barium carbonate. After filtration the clear solution on evaporation gave a deposit of a crystalline barium salt. The composition of this compound is now being determined.

In conclusion, I desire to express my thanks to Miss Mary B. Breed and Miss Lucy Francisco for their careful work in making the analyses and in assisting me in the experiments described in this paper.

BRYN MAWR COLLEGE CHEMICAL LABORATORY,
March, 1896.

THE ACTION OF UREA AND SULPHOCARBANILIDE ON CERTAIN ACID ANHYDRIDES.

BY FREDERICK L. DUNLAP.

In 1882, Piutti,[1] in an article on "urea and thiourea derivatives of phthalic acid," showed that phthaluric acid was the product of the reaction of urea on phthalic anhydride when equal molecules were heated to 110–120°. At a higher temperature he found that the phthaluric acid decomposed into phthalimide with the liberation of carbon dioxide and ammonia. The two stages in the formation of the imide are shown in the following equations:

$$C_6H_4\begin{cases}CO\\CO\end{cases}O + NH_2CONH_2 = C_6H_4\begin{cases}CONHCONH_2\\COOH\end{cases}.$$

$$C_6H_4\begin{cases}CONHCONH_2\\COOH\end{cases} = C_6H_4\begin{cases}CO\\CO\end{cases}NH + CO_2 + NH_3.$$

[1] Ann. Chem. (Liebig), **214**, 20.

I have found that the reaction passes directly through both stages to the formation of phthalimide if the temperature of the mixture of phthalic anhydride and urea be raised at once to 150°, the imide thus obtained being nearly pure.

Phthalimide.—Ten grams of urea (1 molecule) and 25 grams of phthalic anhydride (1 molecule) were heated in a half liter flask, in an oil-bath, until the bath showed a temperature of 150°. At this temperature the contents of the flask became entirely liquid, and ammonia and carbon dioxide were evolved. After heating at this temperature for several minutes, the contents of the flask suddenly solidified. The solid contents of the flask were then treated with boiling water, to free the phthalimide from any unchanged urea or phthalic anhydride. The phthalimide thus prepared was perfectly white and melted without further purification at 227°. When pure, phthalimide melts at 229° (uncorrected) and upon analysis gave the following results:

0.2058 gram substance gave 0.4915 gram CO_2 and 0.0656 gram H_2O.

	Calculated for $C_8H_5O_2N$.	Found.
C	65.31	65.12
H	3.40	3.54

Obviously, this method is a good one for making phthalimide, as the product obtained is practically pure, and only a few minutes are necessary for its preparation. A 90 per cent. yield was obtained.

In hopes that a new and general method for the preparation of imides could be obtained by the action of urea upon anhydrides, this action of urea was studied further upon dichlormaleïc anhydride, dibrommaleïc anhydride and succinic anhydride.

Dichlormaleïnuric Acid.—When a mixture of equal molecules of dichlormaleïc anhydride was heated in a bath to 70°, the mixture began to melt. When the temperature of the bath was raised to 90–95° and held constant for about five minutes the liquid mixture of anhydride and urea solidified. This temperature of 90–95° was maintained for twenty minutes. The solid product thus obtained was washed with a small quantity of cold water and then recrystallized from

alcohol. It recrystallized from alcohol in transparent prisms having truncated ends, and had a melting-point of 158°. When this pure product—dichlormaleïnuric acid—melts, it gives off gas and again solidifies in the melting-point tube, remelting at 179°, the melting-point of dichlormaleïnimide. It is very sparingly soluble in all the ordinary solvents except water, in which it dissolves when heated. Nearly a 50 per cent. yield was obtained.

0.1917 gram substance gave 0.2415 gram AgCl.

	Calculated for $C_5H_4O_4N_2Cl_2$.	Found.
Cl	31.28	31.15

Dichlormaleïnimide.—Five grams of dichlormaleïc anhydride and 3 grams of urea (equal molecules) were heated in a flask, the temperature of the oil-bath being raised to 110–115°. The contents of the flask were liquid at this temperature, and ammonia and carbon dioxide were freely evolved. After heating for fifteen minutes at this temperature the contents of the flask were allowed to cool, and the solid product washed with a small quantity of cold water. One gram of dichlormaleïnimide remained after this washing. When pure, the dichlormaleïnimide melted at 179°, and upon analysis gave the following results:

0.2136 gram substance gave 0.3700 gram AgCl.

	Calculated for $C_4Cl_2O_2NH$.	Found.
Cl	42.78	42.83

We have here, in the formation of dichlormaleïnimide from dichlormaleïc anhydride and urea, a reaction exactly similar to the one in which phthalimide is formed. The first stage of the reaction consists first in the addition of urea to dichlormaleïc anhydride to produce dichlormaleïnuric acid.

$$\begin{matrix} ClC-CO \\ \| \\ ClC-CO \end{matrix} > O + NH_2CONH_2 = \begin{matrix} ClC-CONHCONH_2 \\ \| \\ ClC-COOH \end{matrix}.$$

This dichlormaleïnuric acid, upon being heated to its melting-point, loses ammonia and carbon dioxide with the formation of dichlormaleïnimide,

$$\begin{matrix} ClC-CONHCONH_2 \\ \| \\ ClC-COOH \end{matrix} = \begin{matrix} ClC-CO \\ \| \\ ClC-CO \end{matrix} > NH + NH_3 + CO_2.$$

Dibrommaleïnuric Acid.—A mixture of equal molecules of urea and dibrommaleïc anhydride were heated in an oil-bath. When the bath registered 90° the contents of the flask began to melt. The temperature was raised to 100–105°, at which point it was kept until the liquid contents of the flask had become solid again. After cooling, this solid product was washed with water and purified by recrystallization from alcohol. When pure it is perfectly white and melts at 191° with gas evolution. After melting, the liquid contents of the tube resolidified and again melted at 221°, which is 4° low for the melting-point of dibrommaleïnimide. This low melting-point is explained by the fact that the dibrommaleïnuric acid, upon melting, does not entirely break down into ammonia, carbon dioxide, and dibrommaleïnimide, as is seen by the darkening of the contents of the melting-point tube. The presence of impurities would naturally tend to lower the melting-point of the dibrommaleïnimide. Nearly a 50 per cent. yield of dibrommaleïnuric acid was obtained. If crystallized in bunches of small prisms having doubly truncated ends.

0.2117 gram substance gave 0.2512 gram AgBr.

	Calculated for $C_4H_4Br_2N_2O_4$.	Found.
Br	50.63	50.51

I found this acid to be readily soluble in acetone ; tolerably soluble in chloroform and ether ; insoluble in ligroïn, benzol, carbon bisulphide and water.

Dibrommaleïnuric acid corresponds exactly to dichlormaleïnuric acid, being formed by the addition of urea and dibrommaleïc anhydride.

$$\begin{matrix} BrC-CO \\ \| \quad >O \\ BrC-CO \end{matrix} + NH_2CONH_2 = \begin{matrix} BrC-CONHCONH_2 \\ \| \\ BrC-COOH \end{matrix}.$$

Dibrommaleïnimide.—When equal molecules of dibrommaleïc anhydride and urea were heated up gradually to 135°, the mass turned very dark in color and ammonia and carbon dioxide were evolved. After the evolution of gas had ceased, the then solid contents of the flask were extracted with hot alcohol, filtered from the insoluble portion, treated with bone-black, and then evaporated to small bulk, and the dibrommaleïnimide allowed to crystallize out. It was further purified

by crystallization from alcohol. No analysis of this dibrommaleïnimide was made, because its crystalline form, melting-point and method of formation were definite enough for identification. A twenty-four per cent. yield was obtained.

The formation of dibrommaleïnimide from dibrommaleïc anhydride and urea is exactly similar to the formation of dichlormaleïnimide when urea and dichlormaleïc anhydride are used, therefore no new equations are necessary to represent this imide formation.

Succinimide.—Ten grams of succinic anhydride and 6 grams of urea were heated in a distilling-flask. As the temperature rose the contents of the flask melted and, finally, began to darken, ammonia and carbon dioxide being freely evolved. As the temperature was raised a slightly yellowish distillate, boiling above 280°, was obtained. This distillate immediately solidified and was further purified by recrystallization from anhydrous acetone. It had a melting-point of 124° and was perfectly white. A 40 per cent. yield of succinimide was obtained. Upon analysis it gave the following result:

0.2099 gram substance gave 0.3751 gram CO_2 and 0.1019 gram H_2O.

	Calculated for $C_4H_5O_2N$.	Found.
C	48.49	48.73
H	5.05	5.39

Pike, who first made succinuric acid,[1] states that it melts with complete decomposition. In hopes of finding succinimide as one of these products of decomposition, succinic acid was prepared according to Pike's method, and upon purification was found to have a melting-point of 211–211°.5, and not 203–205°, as Pike gives it. When pure succinuric acid was subjected to distillation it acted as did the mixture of succinic anhydride and urea. The succinuric acid melted with the evolution of ammonia and carbon dioxide, and turned quite dark. A distillate, boiling above 280°, was obtained, which was easily identified as succinimide.

Having obtained succinimide from succinuric acid, this shows us how the succinimide is formed by the action of urea upon succinic anhydride. When this mixture is heated succinuric

[1] Ber. d. chem. Ges., 6, 1104.

acid is first formed. This breaks down at a higher temperature with succinimide, carbon dioxide, and ammonia as its products. The formation of succinimide is represented by the following equations:

$$\begin{matrix} CH_2-CO \\ | \quad >O + NH_2CONH_2 = \\ CH_2-CO \end{matrix} \begin{matrix} CH_2-CONHCONH_2 \\ | \\ CH_2-COOH \end{matrix}.$$

$$\begin{matrix} CH_2-CONHCONH_2 \\ | \\ CH_2-COOH \end{matrix} = \begin{matrix} CH_2-CO \\ | \quad >NH + NH_3 + CO_2. \\ CH_2-CO \end{matrix}$$

Action of Sulphocarbanilide on Phthalic Anhydride.

The action of a substituted urea, sulphocarbanilide, on phthalic anhydride was next studied. It was hoped that a diphenylthiophthaluric acid might be obtained in this way, and the evidence goes to show that it was formed, but that decomposition ensued immediately at the temperature of the reaction. I found as product of the reaction at 125–130°, phthalanilic acid and phenyl mustard oil. The formation of the phthalanilic acid can best be explained by the following equations:

$$C_6H_4\begin{matrix} CO \\ \diagup \\ \diagdown \\ CO \end{matrix}>O + NHC_6H_5CSNHC_6H_5 =$$

$$C_6H_4\begin{matrix} CONC_6H_5CSNHC_6H_5 \\ \diagup \\ \diagdown \\ COOH \end{matrix}.$$

$$C_6H_4\begin{matrix} CONC_6H_5CSNHC_6H_5 \\ \diagup \\ \diagdown \\ COOH \end{matrix} =$$

$$C_6H_4\begin{matrix} CONHC_6H_5 \\ \diagup \\ \diagdown \\ COOH \end{matrix} + SCNC_6H_5.$$

At 170–175° phthalanil, carbonic oxysulphide, and aniline are the products.

Phthalanilic Acid.—Five grams of phthalic anhydride and 7.7 grams of sulphocarbanilide, equal molecules, were heated in an oil-bath until the bath showed a temperature of 125–130°. The contents of the flask liquified, and, after a few minutes heating, began to solidify. The heating was carried on at 125–130° for twenty minutes more. During this heating a very small amount of carbonic oxysulphide was evolved.

The solid product was then washed with a small amount of cold alcohol and the product thus obtained purified by recrystallization from alcohol. The pure product melted at 169–169°.5, and then gave off gas, resolidifying in the melting-point tube, and remelting at 204°, the melting-point of phthalanil. The first alcoholic washings contained quantities of phenyl mustard oil, which was identified by its boiling-point and other properties. After the first treatment with alcohol the product was perfectly white and nearly pure. A 60 per cent. yield was obtained. The phthalanilic acid so prepared crystallized from alcohol in small prisms, and upon analysis gave the following results:

0.2090 gram substance gave 0.5366 gram CO_2 and 0.0865 gram H_2O.

	Calculated for $C_{14}H_{11}O_3N$.	Found.
C	69.71	70.03
H	4.56	4.60

Phthalanilic acid is insoluble in benzol and chloroform; very sparingly soluble in acetone; insoluble in ligroïn and ether; practically insoluble in cold water, but slightly soluble in boiling water, from which it separates upon cooling.

Phthalanil.—Five grams of phthalic anhydride and 7.7 grams of sulphocarbanilide were heated upon an oil-bath to 170–175°. This mixture at first melted, resolidified and remelted with the evolution of carbonic oxysulphide. After heating at 170–175° for ten or fifteen minutes the gas evolution had practically ceased. After cooling, the product was washed with cold alcohol and practically pure phthalanil was obtained. The yield was 93 per cent.

Phthalanil crystallizes from alcohol in long slender prisms and melts at 204°. Laurent and Gerhardt[1] give its melting-point at 203°, and Döbner as 205°.[2]

The first alcoholic washings contain aniline in considerable amount. Upon analysis, phthalanil gave the following results:

0.2464 gram substance gave 0.6790 gram CO_2, and 0.0952 gram H_2O.

[1] Jsb., 1847-48, 605. [2] Ann. Chem. (Liebig), 210, 267.

	Calculated for $C_{14}H_9O_2N$.	Found.
C	75·34	75.16
H	4.04	4·29

Phthalanil is formed in two ways in this reaction, one of which doubtless depends upon the formation of an unstable diphenylthiophthaluric acid, which breaks down at the temperature of the reaction, as follows :

$$C_6H_4\begin{cases}CONC_6H_5CSNHC_6H_5\\COOH\end{cases} =$$

$$C_6H_4\begin{cases}CO\\CO\end{cases}NC_6H_5 + COS + C_6H_5NH_2.$$

The second reaction in which phthalanil is formed depends upon the production of phthalanilic acid by the action of the phthalic anhydride on sulphocarbanilide. The phthalanilic acid so formed breaks down, upon heating, into phthalanil and water.

$$C_6H_4\begin{cases}CONHC_6H_5\\COOH\end{cases} = C_6H_4\begin{cases}CO\\CO\end{cases}NC_6H_5 + H_2O.$$

The phthalanil seems to be formed mostly according to the equation in which carbonic oxysulphide and aniline are by-products.

Laurent and Gerhart[1] first obtained phthalanilic acid by the action of ammonia on phthalanil. They give its melting-point at 192°, at which temperature phthalanil is formed. Zincke and Cooksey[2] obtained phthalanilic acid by the action of alkalies on phthalanil. They found its melting-point to be 158°, at which temperature the phthalanilic acid decomposed with the formation of phthalanil.

Recently, F. Thorp[3] obtained phthalanilic acid by the action of hydroxylamine upon orthobenzoylbenzoic acid. Thorp also gives its melting-point as 191–193°, at which temperature he too finds that phthalanilic acid is converted into phthalanil. Phthalanilic acid made by the interaction of phthalic anhydride and sulphocarbanilide, has, according to my observation, a melting-point of 169–169°.5, at which temperature

[1] Jsb., 1847-48, 605. [2] Ann. Chem. (Liebig), **255**, 375.
[3] Ber. d. chem. Ges., **26**, 1262.

water vapor is given off, the contents of the melting-point tube resolidifying and remelting at 204°, the melting-point of phthalanil.

I have repeated the work of Laurent and Gerhardt, and the melting-point of phthalanilic acid, prepared according to this method, I find not to be 192° but 169–169°.5. Phthalanilic acid was also prepared according to Anschütz's[1] method, by dissolving molecular quantities of aniline and phthalic anhydride in dry chloroform and allowing the mixture to stand, phthalanilic acid separating in a short time from this solution. Prepared according to this method, I find that phthalanilic acid has the melting-point 169–169°.5.

Action of Sulphocarbanilide on Succinic Anhydride.

Succinanil.—Five grams of succinic anhydride and 11.4 grams of sulphocarbanilide (equal molecules) were heated in an oil-bath until the bath registered a temperature of 150–155°. The contents of the flask liquified, and a regular evolution of carbonic oxysulphide took place. After heating at this temperature for 30 to 35 minutes, the contents of the flask had become practically solid. This solid product was then washed with cold alcohol to free it from the aniline which was formed as a by-product. It was then heated with boiling alcohol, and the difficultly soluble portion filtered off. Upon cooling, succinanil separated from the filtrate. A yield of 90 per cent. of succinanil was obtained. The difficultly soluble portion had a melting-point of 226°. When pure, the succinanil melted at 150°, which agrees with the melting-point obtained by Hübner.[2] Upon analysis it gave the following results:

0.2043 gram substance gave 0.5156 gram CO_2 and 0.1031 gram H_2O.

	Calculated for $C_{16}H_9O_2N$.	Found.
C	68.58	68.84
H	5.14	5.60

When succinic anhydride and sulphocarbanilide reacts at 130–135°, succinanil and the compound melting at 226° are formed, phenyl mustard oil being formed at the same time. At this temperature, the yield of succinanil was small. If,

[1] Ber. d. chem. Ges., **20**, 3214. [2] Ann. Chem. (Liebig), **209**, 373.

however, the reaction is carried on at 150–155°, succinanil, carbonic oxysulphide, and aniline are practically the sole products. The formation of succinanil at this temperature is doubtless parallel to the formation of phthalanil from phthalic anhydride and sulphocarbanilide. The formation of succinanil may be explained by the following equations:

$$\begin{matrix} CH_2-CO \\ | \\ CH_2-CO \end{matrix} > O + NHC_6H_5CSNHC_6H_5 =$$

$$\begin{matrix} CH_2-CONC_6H_5CSNHC_6H_5 \\ | \\ CH_2-COOH \end{matrix}$$

$$\begin{matrix} CH_2-CONC_6H_5CSNHC_6H_5 \\ | \\ CH_2COOH \end{matrix} = \begin{matrix} CH_2-CO \\ | \\ CH_2-CO \end{matrix} > NC_6H_5 + COS + C_6H_5NH_2.$$

Succinanilic acid has not as yet been isolated, and I have been as yet unable to identify the compound melting at 226°.

I shall study further the action of urea, sulphourea, sulphocarbanilide, and other substituted ureas upon acid anhydrides.

THE KENT CHEMICAL LABORATORY OF YALE UNIVERSITY.

REVIEWS.

ELECTROCHEMIE. IHRE GESCHICHTE UND LEHRE. BY W. OSTWALD. Large 8vo. 1151 pp. Veit and Comp. Leipzig: 1895. Price, 28 marks.

The recent completion of Ostwald's large work upon Electrochemistry adds an important contribution to scientific literature, for in it we find combined the historical studies and much of the independent research of a man whose fruitful scientific activity has been largely in electrochemical domain. The general plan pursued in the construction of the work is most admirable, for it aims at giving an account of the development of one particular branch of science as a matter of history, and the presentation is made vivid by the incorporation of copious extracts from the original papers in which the results of investigation have appeared. The treatment is therefore a comprehensive one and makes a large book.

The opening chapter is concerned with the slight chemical effects produced by frictional electricity, such as the decomposition of water and of metallic oxides and the formation of nitric acid in moist air. Observations of this kind were made in the latter half of the eighteenth century. This general in-

troduction leads to the "animal electricity" of Galvani (1791), and the construction by Volta in 1800 of the voltaic pile; and we then find treated the development of electrometry up to the invention of Coulomb's tension balance, the first proposition of a "chemical theory" of electrical action by Ritter, the experimental study of electrolytic decompositions and the discovery of the alkali metals, and the electrochemical theories of Davy and Berzelius. The electromagnetism of Oersted (1820), the thermoelectric currents of Seebeck (1821), and Ohm's law next appear upon the program; and they are followed in turn by the long conflict between the contact theory and the chemical theory of the pile, and by the brilliant experimental researches of Faraday. The next strikingly important feature of the history is the appearance of the energy method in physical science about the middle of this century, with the accompanying discoveries of Joule, W. Thomson and Helmholtz; and the reader then passes to the systematic progress which was slowly made in the study of the electrical conductivities of solutions, and in that of the electromotive forces of voltaic combinations. The hypothesis of an electrolytic dissociation and the application made of it in the development of a theory of the cell close the work. These matters are all treated in a clear and vigorous way, the comment made upon the details of historical development are everywhere acute and lucid, (a delightful illustration of this is the review of Kekulé's work upon the electrolysis of the salts of organic acids, p. 1052), and the flowing style of the writing makes the book readable to a degree. This latter characteristic is not, however, always present in the interspersed quotations, as is amusingly apparent in a passage on p. 418, where we meet an astonishing sentence of one hundred and twenty-six words.

Now this book, notwithstanding its many excellent features, presents some serious defects, and the most prominent of these is a lack of balance in the treatment of material. When at the outset all possible details seem drawn into the text and the literature is abstracted with a completeness nothing less than remarkable the reader is caused to anticipate a most satisfying thoroughness of historical exposition in what is to follow. And this anticipation is strengthened by the appearance of no less than forty-two very large pages (Chapter VIII) devoted to the divining rod and similar affairs. After such preparation it is disappointing to find the immensely instructive and important work of Willard Gibbs represented by little more than a single extract from Gibbs' paper, with entire omission of the mathematical formation of his theory; and to find a little later the classical papers of Helmholtz of

about the same date treated in a similarly superficial manner. One might think that a detailed consideration of the progress due to these two men should seem fully as important as a like treatment of galvanic cures, and of the literature of the divining rod.

And, again, it is constantly insisted upon throughout the text that the osmotic pressure theory of the voltaic cell is as quantitative theory the one thing to which the entire discussion leads, for the sake of which even some of Helmholtz's exact work is omitted (p. 1005), and that it is to be regarded as the fit culmination of a century of effort. We are told plainly (p. 1140) that this "Complete theory of the galvanic phenomena . . . corresponds everywhere to the facts, and in the entire range of observations in this much cultivated domain has left almost nowhere an essential residue." In view of the fact that the osmotic theory holds only qualitatively for any practical cell in ordinary use it seems unfortunate that the reader should be referred to another book (p. 1140) for its detailed exposition and therefore for the quantitative confirmation upon which our author's confidence must rest. The present osmotic theory is beyond question a great step in advance, but it is certainly not the ultimate achievement which Ostwald claims it to be.

Objection might also be made to Ostwald's attitude towards the energy doctrine, for the reason that his conception of the substantiality of energy falls so far short of the wider view that the energy doctrine is in essence a scientific *method*, but his position has already been attacked in the current literature with such vigor that this passing reference is sufficient. The book as a whole is an able production and is sure to be of great service; in most respects it is an authoritative work, and no one who takes electrochemical matters at all seriously can afford to be without it.

J. E. Trevor.

The Dilution Law.

It is a well known fact that the dissociation of electrolytes in solution increases with the dilution. If an expression could be found for the relation between dissociation and dilution, this would enable us to calculate the amount of dissociation of any substance, at any dilution, in a given solvent, knowing the dissociation of that substance at any other dilution in the same solvent. The importance attached to the discovery of such a relation is self-evident.

The dilution law of Ostwald[1] is an attempt to state just this relation. That the significance of the law may be seen, it is necessary to follow the more important steps which led to its

[1] Ztschr. phys. Chem., 2, 36 and 278.

deduction. If water solutions of electrolytes are dissociated, and obey the gas laws, then the laws which hold for *dissociating* gases must apply to solutions. If a gas molecule dissociates into two molecules, and the temperature is constant and neither product of the decomposition is present in excess, the following equation holds good :[1]

$$\frac{p}{p_1^2} = C \quad \text{I.}$$

This means that the pressure p, of the undecomposed parts, bears a constant relation to the square of the pressure of the decomposition products p_1. The case with solutions, which is strictly analogous to the above process of dissociation in a gas, is that of a binary electrolyte dissociating into an equal number of anions and cations.

At a given temperature the pressure of a gas is proportional to its mass u, and inversely proportional to its volume v. For the gas pressure we can substitute the osmotic pressure of solutions, which, for the same number of molecules in a given space, is equal to it. For solutions we have then p proportional to $\frac{u}{v}$, and p_1 to $\frac{u_1}{v}$. Substituting these values for p and p_1 in I, we have

$$\frac{uv}{u_1^2} = C \quad \text{II.}$$

The amount of dissociation in a solution, represented by u_1, is the ratio between the conductivity when the dissociation is complete, $\mu\infty$, and the conductivity at any given dilution, μv.

$$u_1 = \frac{\mu v}{\mu\infty}.$$

The non-dissociated portion of the electrolyte in the solution is represented by u.

$$u = 1 - \frac{\mu v}{\mu\infty}.$$

Substituting these values of u and u_1, for u and u_1, in equation II, we obtain,

$$\frac{\mu\infty\,(\mu\infty - \mu v)}{\mu v^2}\, v = C \quad \text{III.}$$

This last equation can be simplified by expressing $\frac{\mu v}{\mu\infty}$ by α, whence it becomes

$$\frac{\alpha^2}{(1-\alpha)v} = C,$$

which is the Ostwald dilution law. In this expression, α is

[1] Ostwald's Lehrb., 1st Edition, 2, 723.

the amount of dissociation in any given solution of an electrolyte; v is the volume in liters of that solution, which contains a gram molecular (or gram equivalent) weight of the electrolyte, and C is a constant.

Having deduced the law theoretically, it remained to apply it to the experimental facts. This was done by Ostwald in his extensive study of the conductivity of solutions of organic acids,[1] involving between two and three hundred compounds. A few of Ostwald's results are given in the following table.

μv is the molecular conductivity.

$\frac{\mu v}{\mu \infty} = \alpha$ is the amount of the dissociation in percentage.

Acetic Acid.

v.	μv.	$\frac{\mu v}{\mu \infty}$	C.
8	4.34	1.193	0.00180
16	5.10	1.673	0.00179
32	8.65	2.38	0.00182
64	12.09	3.33	0.00179
128	16.99	4.68	0.00179
256	23.82	6.56	0.00180
512	32.20	9.14	0.00180
1024	46.00	12.66	0.00177

$\mu \infty = 364$.

o-Amidobenzoic Acid.

v.	μv.	$\frac{\mu v}{\mu \infty}$	C.
64	7.21	2.03	0.00066
128	10.73	3.02	0.00074
256	16.11	4.54	0.00084
512	23.52	6.62	0.00092
1024	33.51	9.44	0.00096

$\mu \infty = 355$.

The values obtained for C, for most of the acids studied, approached a constant, as is seen in the results for acetic acid; yet, deviations of very considerable dimensions are frequently to be found, as is observed in the case of *o*-amidobenzoic acid. It may, however, be said in general, that the law holds approximately for the organic acids, which, in comparison with the inorganic acids, bases and salts, are weakly dissociated compounds.

The dilution law acquires new interest from this work of Ostwald, in that the constant is a characteristic of the compound in question; the numerical value of this constant giving us an insight into many of the properties of the acid. For details on this point the reader must consult the original papers.

[1] Ztschr. phys. Chem., **3**, 170, 241, 369.

The work of Bredig[1] on the conductivity of ammonia, the amines and other weakly dissociated bases, shows the applicability of Ostwald's formula to somewhat more than thirty of these compounds. A few examples are given below:

Ammonia.		*Trimethylamine.*		*Piperidine.*	
v.	*C.*	*v.*	*C.*	*v.*	*C.*
8	0.0023	8	0.0069	8	0.157
32	0.0023	32	0.0075	32	0.162
64	0.0023	64	0.0076	64	0.150
256	0.0024	256	0.0074	256	0.152

The values for C, for each compound, are rather nearer a constant in the work of Bredig on the weak bases, than in that of Ostwald on the organic acids.

While the dilution law as deduced by Ostwald holds thus fairly well for weakly dissociated compounds, it does not apply at all satisfactorily to the strongly dissociated electrolytes—the strong acids and bases, and salts of these acids and bases. A satisfactory reason for this failure on the part of the law, has not yet been furnished.

A very interesting contribution to this subject came recently from Rudolphi.[2] A study of the conductivity of solutions of silver nitrate, of varying concentrations, brought out the following suggestive relations. Representing again by v, the volume of the solution in liters, which contains a gram molecular weight of the salt, and by C, the constant in the Ostwald equation, the following values were found:

When $v = 16$, $C = 0.26$
" $v = 64$, $C = 0.13$
" $v = 256$, $C = 0.065$

At a glance, these figures will show that a constant would be obtained for C, if the individual values of C were multiplied by the square root of v, in each case thus:

$$0.26 \times \sqrt{16} = 0.13 \times \sqrt{64} = 0.65 \times \sqrt{256}.$$

We must substitute then for v in the Ostwald expression the square root of v, when the equation becomes

$$\frac{\alpha^2}{(1-\alpha)\sqrt{v}} = C.$$

To show how well the facts fit in with this formula in this particular case, some of Rudolphi's figures for silver nitrate at different temperatures are given. The letters v and C have the same significance as in Ostwald's results.

[1] Ztschr. phys. Chem., 13, 289. [2] Ztschr. phys. Chem., 17, 385.

T = 25°.		T = 40°.		T = 60°.	
v.	*C.*	*v.*	*C.*	*v.*	*C.*
16	1.00	16	1.03	16	1.11
32	1.08	32	1.18	32	1.15
64	0.96	64	1.07	64	1.14
128	1.03	128	1.05	128	1.16
256	1.05	256	1.19	256	1.16
512	1.07	512	1.27	512	1.15

This table shows that the value of C is nearly a constant, depending slightly, if at all, upon the volume and the temperature.

Rudolphi applied his equation to between fifty and sixty strongly dissociated compounds, calculating in each case the value of α from the conductivity measurements of Kohlrausch, Ostwald and others. The values found for C for the different dilutions of any one substance, approached a constant. A few results will suffice to illustrate the point.

Hydrochloric Acid.		*Potassium Sulphite.*		*Potassium Acetate.*	
v.	*C.*	*v.*	*C.*	*v.*	*C.*
2	4.36	2	0.453	2	1.24
4	4.45	8	0.454	100	1.19
8	5.13	32	0.455	1000	1.18
16	5.13	128	0.544	10000	1.03

Deviations from a constant value for C are not wanting; yet, Rudolphi's equation gives for most of the strongly dissociated substances as near a constant for the different dilutions as Ostwald's equation, when applied to the less dissociated organic acids.

Rudolphi has shown further that this equation holds for different temperatures:

Magnesium Sulphate.

T = 18°.		T = 50°.3.		T = 99°.4.	
v.	*C.*	*v.*	*C.*	*v.*	*C.*
4	0.096	4	0.073	4	0.058
16	0.103	16	0.078	16	0.060
64	0.124	64	0.091	64	0.070

The *numerical value* of the constant for any given compound depends, however, somewhat upon the temperature.

We thus seem to have two expressions for the relation between the dissociation of electrolytes and the dilution of the solutions; first, that of Ostwald,

$$\frac{\alpha^2}{(1-\alpha)v} = C,$$

applying to the weakly dissociated electrolytes; second, that of Rudolphi,

$$\frac{\alpha^2}{(1-\alpha)\sqrt{v}} = C,$$

holding for those substances which are most strongly dissociated. The physical significance of the $\sqrt{v}$ in Rudolphi's equation, instead of v in that of Oswald, is at present unexplained.

Rudolphi's expression has undergone still further modification very recently in the hands of van't Hoff.[1] If in Ostwald's equation, we write instead of α, its value $\frac{\mu v}{\mu \infty}$, the equation becomes,

$$\frac{\left(\frac{\mu v}{\mu \infty}\right)^2}{\left(1 - \frac{\mu v}{\mu \infty}\right) v} = \text{const.}$$

$\frac{\mu v}{v \mu \infty}$ is the concentration of the ions $= C_i$.

$\frac{1 - \frac{\mu v}{\mu \infty}}{v}$ is the concentration of undecomposed salt $= C_m$.

If Rudolphi's expression is changed to

$$\frac{\left(\frac{\mu v}{\mu \infty}\right)^{\frac{3}{2}}}{\left(1 - \frac{\mu v}{\mu \infty}\right)\sqrt{v}} = \text{const.}, \text{ or } \frac{\left(\frac{\mu v}{\mu \infty}\right)^3}{\left(1 - \frac{\mu v}{\mu \infty}\right)^2 v} = \text{const.}$$

and we substitute in the last form C_i and C_m for their respective values, we obtain the very simple relation:

$$\frac{C_i^3}{C_m^2} = \text{const.}$$

The physical meaning of this expression is as little known as that of Rudolphi's expression. Van't Hoff, however, calls attention to the greater simplicity of his equation, and shows by a number of examples, that it agrees a little more nearly with the facts, for strongly dissociated compounds than does the equation of Rudolphi.

Kohlrausch[2] has still further simplified, algebraically, the last very simple expression in the following manner. If we write this in the form, $\frac{C_i}{C_m} = \frac{\text{const.}}{C_m^{\frac{1}{3}}}$

observing that $C^{\frac{1}{3}}$ is the linear concentration of the molecules, and its reciprocal, $C^{-\frac{1}{3}}$, the mean distance of the molecules, we see that $\frac{C_i}{C_m} = \text{const. } r_m$, in which $r = C^{-\frac{1}{3}}$.

This, as Kohlraush observes, "would be, without doubt, a surprisingly simple relation."

[1] Ztschr. phys. Chem., **18**, 300. [2] Ztschr. phys. Chem., **18**, 662.

JOHNS HOPKINS UNIVERSITY. HARRY C. JONES.